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Rayon Reports

Prepared Monthly by American Viscose Corporation, New York, N.Y. September, 1930

Avisco-Sponsored Study Finds Best Way To Launder Viscose Rayon Dress Shirts

Further evidence of the continuing program of American Viscose Corporation to help manufacturers turn out serviceable rayon products—and help the rayon product merchandiser please his customers—has just been furnished. It is contained in a bulletin released by the American Institute of Laundering.

The bulletin reports on a special A.I.L. study, under a Fellowship sponsored by Avisco, on the launderability of washable rayon dress shirts. It affirms conclusively that the standard formula for laundering cotton dress shirts is also the best for those of rayon.

Suitability of fabric depends on construction

It is emphasized that with rayon shirts (as with practically all garments) the "suitability of a fabric for a given purpose is determined by the cloth construction, the selection of dyestuffs, the method of application and proper handling of goods throughout the finishing operations."

Variables introduced to check standard formula

For the laundering tests about 250 identical shirts of three different standard rayon shirting constructions were made by a nationally known manufacturer. The three materials were a fuji type 100% spun and filament rayon, white; a lightweight spun rayon twill containing 30% cotton, blue; and a 100% spun rayon oxford type fabric, sandune.

The tests, using the standard washing formula for cotton shirts shown in the accompanying table, included washing, extracting and drying in a drying cabinet. Variables were also introduced in each stage of the formula as a check against the standard procedures.

The final phase of the project was a visual comparison of groups of test shirts after machine pressing and folding. Here again it was clearly shown that the best procedure is that employed in handling the usual run of cotton shirts. For a copy of the A.I.L. Bulletin describing these tests, write to American Viscose Corporation.

How To Launder Viscose Rayon Shirts

- For best results on viscose rayon shirts, use washing formula shown here.
- For best results in pressing viscose rayon shirts, use no sizing materials.
- Dress shirts made from well designed and well constructed viscose rayon fabrics, can be finished just like cotton dress shirts. This does not apply to sport shirts. Extract lightly before finishing and finish on regular shirt unit.

Laundering Formula Used For Testing Washability of Viscose Rayon Shirts

Operation	Water Level	Time	Temperature	Supplies	pH
Suds	5 inches	5 min.	95°-100° F.	Neutral Soap	10.0
"	5 "	5 "	" "	" "	10.0
"	5 "	5 "	" "	" "	10.0
Rinse	10 "	3 "	" "		
"	10 "	3 "	" "		
"	10 "	3 "	" "		
Sour	5 "	5 "	" "	Sour	5.0

Extraction: Equipment used was a 30 inch extractor operating at 1,085 R.P.M. The extractor was brought to top speed and shut off.

RAYON 20 YEARS AGO

WASHINGTON, D.C., Sept., 1930—The Department of Agriculture is experimenting with peanut hulls as a possible future source for rayon.

ROME, Sept., 1930—"Cetolina" and "Cesantina" have been suggested to replace the term "artificial silk" in Italy.

NEW YORK, Sept., 1930—Elaborate floral effects are being designed for next spring and summer's rayons.

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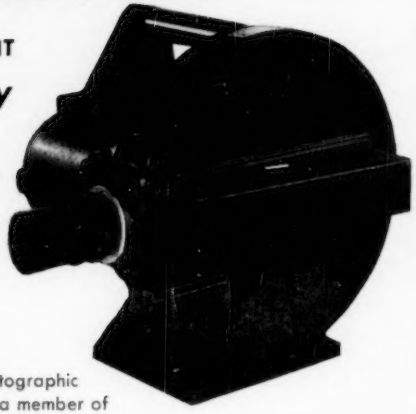
2 GREAT NAMES JOIN HANDS.....

Wollensak

FASTAX

Edward A. Springer, PRESIDENT *Wollensak Optical Company Announces Purchase of Fastax High Speed Camera*



Wollensak Optical Company has purchased outright from Western Electric Company the Fastax High Speed Motion Picture Camera, together with all rights for exclusive manufacture and distribution. By acquiring the Fastax, Wollensak will be able to render an immeasurable service to many industries and scientific laboratories.

The Fastax Cameras, part of our new Industrial and Technical Photographic Division, will be headed by John H. Waddell, for twenty-one years a member of the Technical Staff of Bell Telephone Laboratories. Under his guidance the Fastax was perfected. Mr. Waddell has also been photographic consultant to both the Army and Navy, and was a consultant to the Army Air Force on the Bikini Experiments. He will personally attend to all inquiries regarding the Fastax and to all problems of high speed photography.

E. A. Springer

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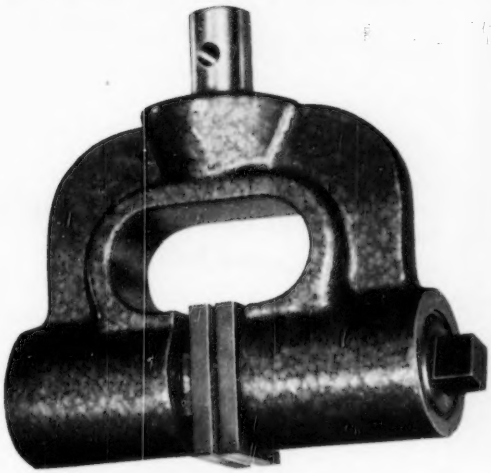

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TEXTILE RESEARCH JOURNAL

VOL. XX, No. 9 September, 1950

The Application of Punched-Card Techniques to Data on the Physical Properties of Single Fibers*

Helmut Wakeham and James H. Wakelin

Textile Research Institute, Princeton, New Jersey

Abstract

The punched-card method is illustrated, with a description of the procedures used in analyzing the data on single cotton fibers. The samples were tested for 7 properties, from which 5 more were derived by computation. For each of these 12 properties there were prepared a histogram showing the distribution of the property values within variety groups, means and standard deviations for 6 subgroups within each variety, and a three-factor analysis of variance of the means for all varieties and subgroups. The steps in obtaining these results from the punched cards are outlined. Some advantages of this method over the desk-calculator approach are discussed.

THE PURPOSE of this paper is to draw attention to the use of punched-card methods in the evaluation of the physical properties of single textile fibers and to present some results which have been obtained at the laboratories of the Textile Research Institute in applying this procedure to the study of cotton and wool fibers.

During the course of the past 12 months, increasing attention has been given to the research on single-textile-fiber properties. The single-fiber work on cotton aims at a better understanding of cotton through a concerted program to evaluate differences in cotton types, the effects imposed upon the physical properties by maturity, and the influence of morphology and treatments on the measured physical properties. Another branch of the cotton program includes research on the progression of physical changes exhibited by cotton during the course of its processing from the bale to the finished cloth. This is a companion project to that in which changes in the degree of polymerization are being followed in cotton from the bale to the cloth by fluidity studies of the cotton cellulose in cupriethylene diamine solutions [18].

* Presented in part by Dr. Wakelin at the Meeting of The Fiber Society, Fontana Village, N. C., April, 1950.

In the internationally sponsored Wool Research Project,* single-fiber testing of wool fibers is a major component of the work. The program includes in part the comparison of samples of New Zealand and Australian wools against matched domestic wools. These wools are being followed through industrial processing to study the changes occurring in the physical properties of the fibers and to study the effects of "resting" or ageing the wool at selected stages in its manufacture.

The testing and analysis of the physical properties of single fibers, both in the fields of cotton and wool, have always been time-consuming operations. A rapid appraisal of the laboratory testing procedure indicated that it probably would not be possible to decrease by more than a factor of two the time required for the acquisition of data from force-elongation curves and from other experimental procedures. Furthermore, an examination of the computational procedure, using the most modern key-driven calculators, showed clearly that the reduction and analysis of the physical data required five- to ten-fold the time necessary for acquisition of that information in the laboratory. This time was consumed by such routine arithmetical functions as those involved in computing fiber diameters, breaking stresses, group means, and standard deviations; in selecting certain classes of fibers for comparison with others; or in making a statistical factor analysis.

Doubtless, the reason why more research is not undertaken in the single-fiber field is a direct result not so much of the arduous experimental methods involved but of the long and tedious operations which must be performed before the data are available in meaningful form for analysis and interpretation.

It was felt, therefore, that the single-fiber programs on both cotton and wool could be accelerated materially if the transcription, calculation, sorting, statistical analysis, and final printing of the data could be mechanized to decrease the time-consuming manual labor included in desk-calculator operation and in data handling. It was also recognized that if such a medium were found it would undoubtedly solve the pressing problem of the storage of data in convenient and easily accessible form. The use of punched-card equipment was immediately obvious as one method for meeting most of these requirements. Accordingly, with the assistance of Princeton University, the Educational Testing Service of Princeton, and the International Business Machines Corporation, the punched-card technique was given a trial on the data derived from 600 single cotton fibers of four varieties, and over 200 single wool fibers of two main types. The results of these tests will be presented in this paper, together with estimates of the time saved in the use of punched-card techniques in the single-fiber field.

The Punched-Card Method

Punched-card methods have for the past 20 years been applied actively to problems in scientific research [15], including the solution of partial and total differential equations [11, 12], the analysis of complex spectra [1, 17], molecular-structure determinations [19], astronomical calculations [5, 8], construction and printing of mathematical tables [4, 6, 10], and statistics [2, 3, 14, 16]. Methods of using the punched-card techniques have been reviewed by Eckert [9].

In the I.B.M. punched-card system,* information is punched in cards containing 80 columns and 12 rows (Figure 1). One decimal digit (0-9) may be punched in any one column; the use of the "x" and "y" rows above the main printed portion of the card is useful for special digit coding and for alphabetic characters.

The original data are punched in cards by means of a manually operated card punch. Because this step is subject to errors of the operator, it is desirable that the amount of material punched by hand be kept to a minimum and that the information on the cards be verified. A verifier is available to aid in this last step. The original punched cards are introduced to the verifier, and the operator presses those keys which correspond to the sequence of punched data on the original card. If there is a mismatch, the verifier locks into position so that the operator may investigate the source of the error. A good operator can punch and verify cards at the rate of 100 per hour or better.

The punched cards are then handled by standard business machines which are capable of performing the essential card manipulations, such as sorting into

* Sponsored by The Wool Bureau, Inc., acting for the International Wool Secretariat and the American Wool Council; the U. S. Dept. of Agriculture; the Office of Naval Research of the Navy Department; and a number of American wool manufacturers.

* The punched-card system used in this work was that of the International Business Machines Corporation because such equipment was available to the Institute. Other systems may for many purposes be used with equal satisfaction.

orders and groups, card counting, matching, and reproducing and data tabulating. More important for scientific purposes, these machines can add, subtract, multiply, and divided numerical quantities punched in the cards.

The business-machine equipment reads the information punched in each card by brushes which make electrical contacts through the holes as the card runs through the machine. The types of machines which are available for performing these operations are discussed below.

Counting Sorter

This machine separates cards at the rate of 400 per minute into groups, depending on the value of a digit in any one column, and counts the number of cards going into each group. It can be used to sort disarranged cards, to arrange them in any desired order, to divide them into subgroups for summarizing, or to pick out any individual card in a group. It is very useful in the examination of property distributions, preparation of histograms, etc.

Reproducer

This is a machine by which all or any part of the information punched in one set of cards can be punched into another set at the rate of 100 cards per minute. It will also transfer punched information from a master card to a group of detail cards. This operation is known as "gang punching."

Calculating Punch

When computations are to be performed with information supplied by the cards, a calculating punch is used. This machine performs additions, subtractions, multiplications, and divisions, either singly or in combination with each other, taking into account the signs of the numbers involved. Constant factors needed in the calculation can be preset into the machine and produced when needed in the operation. It is then not necessary to use up columns of the detail card to supply this information. When the computation is completed, the machine will round off the answers as specified, punch the results in prescribed locations on the card, and indicate on the card the sign of the number punched.

The Type 602-A Calculating Punch is capable of multiplying a 22-digit multiplicand by an 8-digit multiplier to obtain and punch a 30-digit product. Likewise, in division a 15-digit dividend can be divided by an 8-digit divisor to obtain and punch an 8-digit quotient. The storage capacity of the 602-A is 102 digits, and it operates at a speed of 200 cycles per minute. In order to estimate the time required for a given operation, however, that operation must be broken down into machine cycles—*i.e.*, one cycle for reading and storing numbers from the card, one

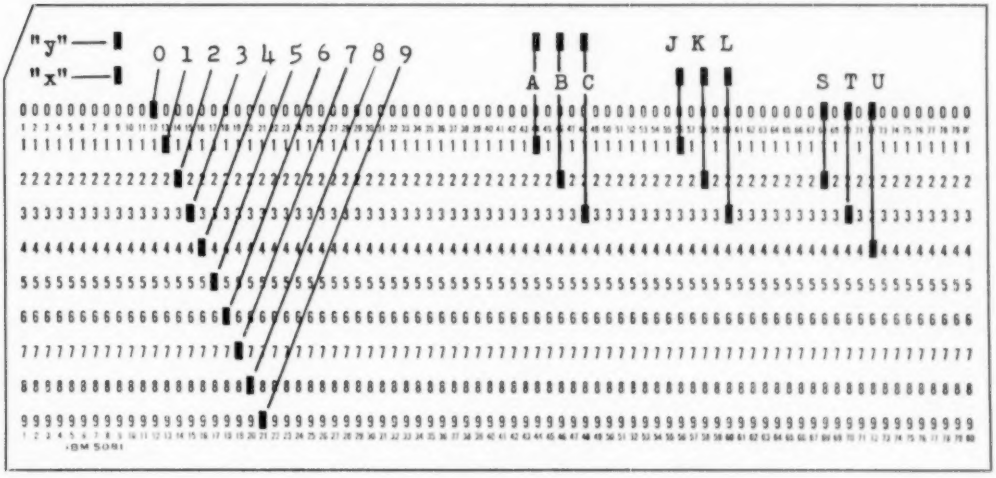

FIG. 1. *Coding used on the I.B.M. punch card.*

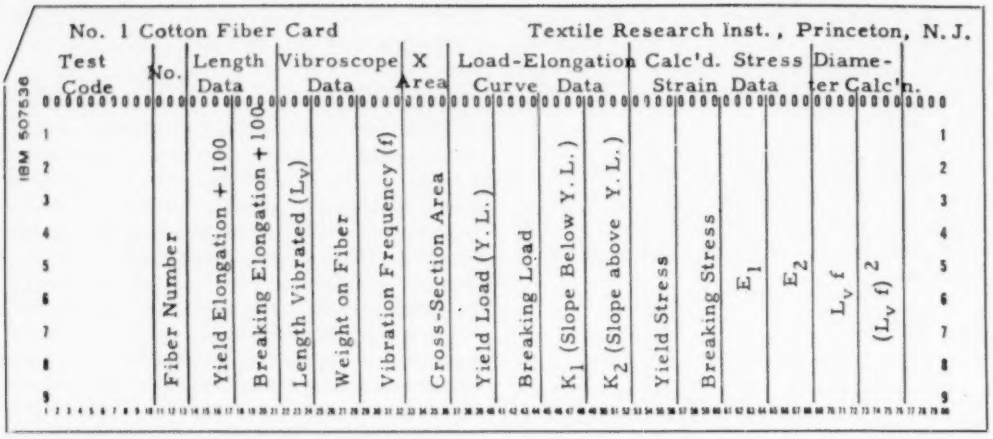

FIG. 2. *Layout of cotton fiber properties on punched card.*

for each step in the operation, one for punching the answer, etc.

Summary Tabulator

At any stage in the operations, the cards can be put through an accounting machine or tabulator wired so that any or all of the information can be printed and summated. Thus, in a group of cards containing X and X^2 values, the tabulator will list the individual quantities at the rate of 80 cards per minute and also print the sums of the Xs and the sums of the X^2s. These sums can also be automatically punched on summary cards by connecting the tabulator with a reproducer. By putting these summary cards through the calculating punch again, it is possible to compute means and standard deviations, which can then be listed by the tabulator to provide tables for statistical analysis.

In short, these machines can perform quickly many operations in handling data which require weeks and months by older methods. All steps in the procedure can be set up in a standardized form so that actual preparation and handling of the cards is done by trained operators. The data are stored on cards which can be taken out, reshuffled, and analyzed to investigate new factors when required.

TABLE I

Fiber characteristics	Properties measured from load-elongation curve	Properties calculated
Length	Elongation to break	Cross-sectional area
Mass per unit length (vibroscope) [13]	Breaking load	Stress to break
Fiber maturity or cross-sectional shape	Yield load	Stress to yield
Location of break	Elongation to yield	
	Slope below yield point	Elastic modulus below Y.P.
	Slope above yield point	Elastic modulus above Y.P.

Application of the Punched-Card Method to Single-Fiber Testing

Cotton Fiber Tests

Table I shows the fiber properties which are measured and calculated for each cotton fiber being tested. Similar properties are also being determined for wool fibers.

In the application of the punched-card technique to manipulation of the test data outlined in Table I, the standardized arrangement of the data on the card is very important. The layout for the cotton-fiber cards is shown in Figures 2 and 3. Three cards were necessary for each single fiber tested, and one card was required for each group and subgroup in the statistical analysis. The No. 1 Card contained the test identification, the measured data, and the calculated area and stress-strain properties for each fiber. For example, in the card shown in Figure 2, columns 1–10 are assigned to test identification and

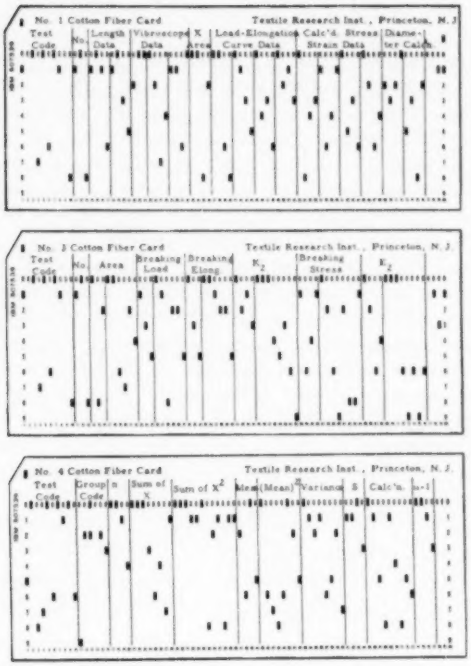

FIG. 3. *Sample punched cards for cotton fiber data. Card No. 1 is similar to that shown in Figure 2. Card No. 2 is similar to Card No. 3, which contains, in addition to identifying information, the values of the property and the property value squared in each of the zones shown. Card No. 4 is a summary card for a given property and group of fibers.*

test conditions, 11–13 to the fiber number, 14–21 to length data, etc. Of the 80 columns in the card, 48 were used for test and fiber identification and for insertion of the load-elongation-curve data and vibroscope measurements. The latter were used in the determination of the cross-sectional area of the fiber by the vibrating-string principle [7, 13].

The No. 2 and No. 3 Cards were each arranged to contain the identifying information and half of the property values punched in the No. 1 Cards. This allowed space on the second and third cards for the squares of the property values required in the statistical study. The layout on these cards is also shown in Figure 3.

The No. 4 Card was arranged to accommodate the number of fibers, the sum of the property values, the sum of the squares of the property values, the

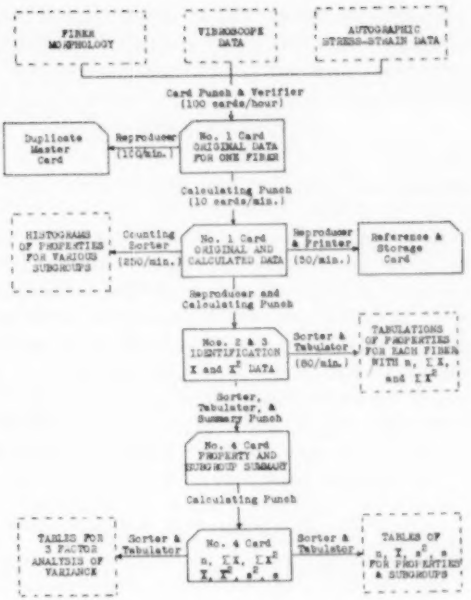
FIBER MORPHOLOGY
VIBROSCOPE DATA
AUTOGRAPHIC STRESS-STRAIN DATA
Card Punch & Verifier (100 cards/hour)
Duplicate Master Card
Reproducer (120/min.)
No. 1 Card ORIGINAL DATA FOR ONE FIBER
Calculating Punch (10 cards/min.)
HISTOGRAMS OF PROPERTIES FOR VARIOUS SUBGROUPS
Counting Sorter (250/min.)
No. 1 Card ORIGINAL AND CALCULATED DATA
Reproducer & Printer (50/min.)
Reference & Storage Card
Reproducer and Calculating Punch
Nos. 2 & 3 IDENTIFICATION X and X^2 DATA
Sorter & Tabulator (60/min.)
TABULATIONS OF PROPERTIES FOR EACH FIBER WITH n, ΣX, and ΣX^2
Sorter, Tabulator, & Summary Punch
No. 4 Card PROPERTY AND SUBGROUP SUMMARY
Calculating Punch
TABLES FOR 3 FACTOR ANALYSIS OF VARIANCE
Sorter & Tabulator
No. 4 Card
Sorter & Tabulator
TABLES OF FOR PROPERTIES & SUBGROUPS

FIG. 4. *Outline of punched-card operations performed in the statistical analysis of single-fiber data.*

mean property value, the square of the mean, the variance, and the standard deviation, along with the group and property identification. It contained summary information for any property-subgroup combination which might be of interest in the analysis of the data.

Outline of Punched-Card Operations

Figure 4 shows an outline of the operations performed on punched cards with the single-cotton-fiber data. The results of the experimental observations were hand-punched and verified on the No. 1 Cards. A master duplicate deck was then made with the reproducer to avoid the necessity of punching a new deck should anything happen to the original one. The cards were then put through a calculating punch five times to compute each of the five derived properties (Table I).

The calculation of the cross-sectional area of the fiber from the vibroscope data is a good example of the type of computation which the calculating punch can handle. The relationship between cross-sectional area (A) and the length (L) of fiber vibrated in the

vibroscope, the weight (W) on the fiber, the density (d), and the frequency (f) at which the fiber vibrates (cycles/sec.) in its fundamental mode is given by the equation

$$A = \frac{980\,W}{4\,d\,(Lf)^2} = \frac{KW}{(Lf)^2}$$

where $K = \frac{980}{4\,d}$ (cm.)^4/g. sec. in c.g.s. units.

The calculating punch can be instructed to perform the computation of A in three operations. The first step is to take the values of L and f from columns 22–24 and 29–32, respectively, and multiply them together to obtain the product Lf, which is punched in columns 69–72. In the second step this product is squared, the answer being punched in columns 73–76. In the final step the factor W (columns 25–28) is divided by the value of $(Lf)^2$ and the quotient is multiplied by the constant term K, which is already stored in the machine. The cross-sectional area, A, is punched in columns 33–36 by the machine after the final step is completed.

After the No. 1 Card had been completed, No. 2 and No. 3 Cards were punched from the No. 1 Cards with the aid of a reproducer. The fields for the various fiber properties on the second and third cards were spaced so that the squares of the property values could also be punched on the same card. This squaring of numbers was performed on the calculating punch at the rate of 7,200 numbers per hour, or two per second. The No. 2 and No. 3 Cards were then sorted into fifteen main and subgroups for each variety and run through the tabulator, which printed lists of the fiber identification and property values for each fiber, along with the sums of the values and of the values squared for each group. At the same time, these summations for each property, along with group identifications, were punched into No. 4 Cards with the reproducer connected to the tabulator as a summary punch. These cards were then put through the calculating punch four times to compute the property means, means squared, variances, and standard deviations for each group. By use of the sorter and tabulator, again two types of tables were printed: (1) tables of means and means squared of the subgroups for an analysis of variance, and (2) tables of means, variances, and standard deviations. Thus, there were obtained from the machines the

TEST AND GROUP CODES	NUMBER OF FIBERS	SUM OF X's	SUM OF $[X]^2$	MEANS	$[MEAN]^2$	VARIANCE
A0070601083K1 11	0015	00005308	000002129812	354	125316	17913
B0970601083K1 11	0007	00002314	000000914324	331	109561	24732
C0070601083K1 11	0010	00005301	000003388167	530	280900	64293
E0870601063K1 11	0011	00003728	000001462718	339	114921	19893
SUBGROUP TOTALS	43	00016651		1554	630698	
A0070601083K1 12	0030	00016701	000010624081	557	310249	45573
B0970601083K1 12	0027	00011730	000006264446	434	188356	45139
C0070601083K1 12	0031	00016616	000010447768	536	287296	51386
E0870601063K1 12	0027	00015253	000009605575	565	319225	37986
	115	00060300		2092	1105126	
A0070601083K1 13	0006	00003581	000002449529	597	356409	62334
B0970601083K1 13	0005	00001990	000000831190	398	158404	9793
C0070601083K1 13	0003	00001847	000001139907	616	379456	1078
E0870601063K1 13	0015	00010163	000007307905	678	459684	29814
	29	00017581		2289	1353953	
GRAND TOTALS	187	00094532		5935	3089777	

FIG. 5. *Sample tabulation of single-fiber summary data for factor analysis.*

fiber data summarized in convenient tabular form for further statistical considerations. (See Figure 5.)

Although the foregoing description of punched-card operations has been with respect to the manipulation of single-cotton-fiber data, very similar procedures are being used with the results of the wool fiber tests. The card layouts are almost identical, with the exception that in one or two instances different properties are assigned to the various fields on the card. A detailed account of the wool fiber application of the punched-card method has accordingly been omitted for the sake of brevity.

Economical Advantages of the Punched-Card Method

In the course of a test operation similar to that described above, an attempt was made to compare the time required to perform the work by the desk-calculator method with that used in the punched-card method. It was estimated that by means of a desk calculator one trained operator could make all the calculations and the statistical analysis of the data on 600 cotton fibers in four variety groups in about 2 months. The time required to achieve the same results by the punched-card method was about 2 weeks. This estimate includes time required to set up the machines, which would be less the next time the operation was carried out. One important advantage of the punched-card method is that the computations are performed without errors. Finding and correcting such errors in desk calculations can be very time-consuming.

In the evaluation of the four basic types of wool under study in the Wool Research Project, it will be necessary to examine at least 100 fibers at each of eight stations, from the grease wool to the finished cloth. Each group of 100 fibers may have to be tested at 65% R.H. and in water at 70°F. This amounts to $400 \times 2 \times 8$, or 6,400 fibers, on each of which at least 10 physical properties, or a total of 64,000 individual items, have to be examined and to which statistical analytical procedures must be applied. At the current level of operation, a complete analysis of 10 fiber properties for 200 fibers required about 2 man-months using the desk-calculator procedure, or 1,000 properties per man-month. On this basis the analysis of the 64,000 properties would require of the order of 5 man-years. The amount of time required by the punched-card technique is about 20% of that required for the desk-calculator method. Therefore, it is expected that in less than 1 year, or possibly 6 months, following the acquisition of the original physical data, the analysis of these 64,000 properties will be completed.

Balanced against the saving in time must be the cost of leasing the punched-card machines.* If the volume of work is sufficiently large, the cost of the punched-card equipment can easily be justified. Many industrial concerns already have much of the necessary equipment in their accounting or sales departments, and the research worker may find it to his advantage to use these machines on research problems when they are idle. Otherwise, it is possible to have the card operations performed at standard rates by the I.B.M. Service Bureau, which has offices in most of the major cities.

Conclusions

The punched-card method for storing and computing research results seems to offer great advantages to single-fiber research work in terms of time and labor saving. Trained technicians can spend the time formerly needed for calculating results in testing more fibers to obtain more and better answers to questions about fiber behavior. The advantages of convenience and speed here observed with punched-card methods for single-fiber tests should be attainable with many other types of textile testing done in large quantity.

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* The International Business Machines Corporation and Remington Rand, Inc., supply their punched-card machines only under a lease arrangement.

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(Manuscript received June 26, 1950.)

Correction

In the article "Review of Research and Development in the Field of Textiles During 1949," which appeared in the May, 1950, issue, in item No. 402 of the Bibliography, page 351, the author's name should be "Best-Gordon" instead of "Best-Bordon."

Item No. 402 is an answer to a Letter to the Editor (*J. Text. Inst.*), reference to which was omitted from the Bibliography. The reference for the original letter is:

Hill, F. R., and Kornreich, E., **Some Observations on the Influence of Fabric Structure on Felting**, *J. Text. Inst.* **40**, No. 10, T733–4 (1949).

Enzymatic Digestion of Protein Fibers

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IN THE STUDY of microbiological degradation of protein fabric and fibers in this laboratory, it has been found that an actinomycete was capable of destroying the strength of wool fabric in a 2-week period under certain cultural conditions. The organism was originally isolated from mildewed wool obtained from the Quartermaster Salvage Warehouse on Biak Island. From biochemical and morphological studies it appears to belong to the genus *Streptomyces*, although its characteristics do not conform to those of any of the species described in the Sixth Edition of *Bergey's Manual of Determinative Bacteriology*. Systematic studies of this group of organisms, impelled by the discoveries of antibiotics, will undoubtedly reveal many new species as well as more complete knowledge of those already described. This organism may fall into either group of actinomycetes. The present study reports that a cell-free proteolytic enzyme preparation obtained by culturing the same actinomycete will also decompose wool and man-made protein fibers.

In most enzyme studies using microorganisms, intact cells rather than cell-free preparations have been employed. Of the cell-free enzyme preparations, those obtained by rupturing the cells have been used frequently. Another approach to the problem is to utilize the cell-free substrate into which the organism has excreted its enzymes. Filterable proteinases of this type, capable of hydrolyzing gelatin and casein, have been derived from organisms such as *Bacillus prodigiosus*, *Bacillus pyocyaneus*, and *Bacillus subtilis* [3, 7, 13].

Gelatin, casein, and denatured albumin have been used to demonstrate the activity of enzymes obtained after autolysis of the cells of *Bacillus thermophilus*, *Bacillus aerothermophilus*, and *Bacillus thermoacidurans* [2]. The gas-forming anaerobes, *Bacillus perfringens*, *Bacillus histolyticus*, and others, have yielded enzymes of narrow specificity for gelatin and gluten, a maximum concentration of which was reached in 3–4-hr. growth of the organisms and on purification showed a 2,000-fold concentration [9].

The mechanism of activation of a proteinase elaborated by *Clostridium histolyticum* has been investigated with purified preparations [8]. Filtrates of *Clostridium welchii* have confirmed the presence of a collagenase (the K toxin) which is capable of disintegrating muscle [1, 12]. From an enterococcus a proteinase lytic for gelatin and casein has been demonstrated [5].

Also it has been shown that group A streptococci produce an extracellular enzyme, proteolytic for type-specific M antigen [4]. Crude proteins from muscle and diazotized proteins derived from skin have been used to titrate the activity of a streptococcal proteinase [14]. From the cultivation of *Streptomyces albus* a proteolytic factor active against the streptococci of groups A, B, C, and G has been utilized to disintegrate streptococci, thereby yielding a carbohydrate suitable for the group determination of the streptococci [10].

Investigations pertaining to the stability of wool and other fibrous proteins have utilized animal enzymes and those of plant origin, such as papain.

Methods

The actinomycete was cultured in 250-ml. amounts of nutrient broth (5 g. peptone, 3 g. beef extract, 1,000 ml. water), pH 7, contained in liter flasks, at 30°C for 30 days. The inoculum consisted of 0.5 ml. of a distilled-water suspension obtained by removing the surface growth from week-old nutrient agar slants. After incubation the cell-free substrate (pH 8.5), obtained by sintered glass filtration, was combined with an equal amount of 0.05*M* potassium phosphate at pH 7. This substrate-phosphate mixture (pH 7.85), hereafter designated as the enzyme preparation, was used without further adjustment.

Six protein materials * in various forms were used for this study: yarns made of wool and of fibers manufactured from protein from casein, corn, and peanut; staple fiber made from soybean protein; and bristles from casein. Some of the manufactured fibers or yarns have found use in various combinations with wool, rayon, cotton, nylon, mohair, and fur, and are of considerable interest from the standpoint of fabric deterioration. The processes of manufacture are different for each fiber, but, in general, they follow a single pattern. After an oil-free meal is obtained from the various raw materials the protein is solubilized by means of alkali. This solution is then extruded through a spinneret into an acid coagulating bath. Subsequently, the fibers are stretched and hardened. The hardening processes are designed to block the reactive groups in the protein, giving the fiber stability.

For this study the fibers were given no treatment other than grinding in a Wiley mill. The particles which passed through a 20-mesh but not through a 40-mesh sieve were used. After conditioning the ground fibers at 70°F and 65% relative humidity,† 100-mg. portions were weighed into small Erlenmeyer flasks. Samples were also weighed for the purpose of determining the nitrogen content of the fibers.

Ten-ml. portions of the enzyme preparation were added to one set of flasks containing the weighed fibers. The fibers in a duplicate set of flasks were suspended in 10-ml. portions of a heat-inactivated enzyme-preparation mixture. The inactivation was carried out at 80°C for 5 min. To prevent bacterial growth, a few crystals of thymol were added to each flask before stoppering. All flasks were incubated at 30°C.

One set of the fibers in the enzyme preparation and the duplicate set in the heated enzyme were withdrawn at the close of each incubation period of 1, 3, 7, 14, and 21 days.

The extent of digestion of the fibers was measured by determining the amount of "nonprotein" nitrogen (nitrogenous material soluble in 0.6*M* trichloroacetic acid) in aliquot portions of the enzyme preparation obtained after removal of the fibers by paper filtration. To each aliquot was added five times its volume of the trichloroacetic acid. The mixture was filtered by suction through medium-porosity sintered-glass crucibles. In protein chemistry the assumption is made that trichloroacetic acid precipitates protein as a salt, leaving the partially and completely digested fragments of the protein in solution. On filtration these "nonprotein" products of digestion—peptones, peptides, and amino acids—were used to estimate the degree of digestion. Five-ml. portions, in triplicate, of this protein-free filtrate were analyzed for nitrogen by the micro-Kjeldahl procedure of Miller and Houghton [11].

Similar determinations were carried out on both the heated and the unheated enzyme preparations.

The percent nitrogen in the fibers was determined by digesting 100 mg. of each fiber. Five-ml. portions of the quantitatively diluted digest were distilled and titrated.

After correction of the results obtained for the nitrogen contributed by the enzyme preparations, the percent digestion of the fibers was calculated for each fiber for each incubation period.

Results and Discussion

In Table I are given the mg. of nitrogen in 100 mg. of fibers conditioned and weighed at 65% relative humidity, 70°F. Under these conditions wool absorbs about 16% of its dry weight in moisture. The moisture contents of casein, soybean, peanut, and corn fibers are approximately 12.6%, 11%, 15%, and 13%, respectively. The casein bristle contains about 10% quinone.

In Figure 1 is shown the percentage of the total nitrogen of the fibers present in the filtrate as nonprotein, as a result of the action of the enzyme preparation. It is apparent from the curves that all the

TABLE I. MILLIGRAMS OF NITROGEN IN 100 MG. OF PROTEIN FIBER*

Wool	15.18
Casein fiber	11.83
Casein bristle	11.62
Peanut	13.45
Soybean	14.33
Corn	13.78

* Fibers were weighed in an atmosphere of 65% relative humidity, 70°F.

* The Bureau is indebted to the Drackett Company, Cincinnati, Ohio, for the soybean fiber, and to Aralac Incorporated, New York, New York, for the casein yarn. The yarns from peanut and corn and the casein bristle were kindly supplied by the Southern, Northern, and Eastern Regional Laboratories of the Bureau of Agricultural and Industrial Chemistry, U.S.D.A.

† The National Bureau of Standards and the American Society for Testing Materials, together with other laboratories, have accepted these conditions as standard for the weighing of textile materials.

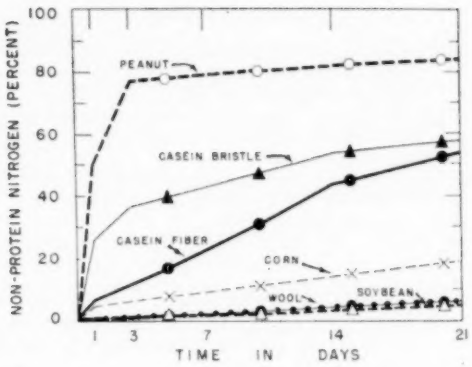

FIG. 1. *Percentage of the nitrogen in the fibers present as nonprotein at indicated time, due to action of enzyme preparation.*

protein fibers, including wool, are attacked by the enzyme preparation, although wool and soybean are digested only slightly. The fibers of casein and corn protein show susceptibility and the slope of the curves indicates progressive deterioration. In contrast, the curves for casein bristle and peanut protein fibers demonstrate marked susceptibility to the enzyme preparation during the early exposure period.

The results of exposing the fibers to the heat-inactivated enzyme preparation are illustrated in Figure 2. Only the peanut fiber and casein bristle show significant dissolution. It should be emphasized that the processes of manufacturing casein bristles are designed to harden the proteins to resist the solvent action of paints and oils, and it is not surprising that they soften in an aqueous medium. It may be noted that casein fiber starts to disintegrate during the third week of exposure to the heat-inactivated enzyme preparation, whereas corn and soybean fibers resemble wool in their resistance to disintegration.

In some unpublished work utilizing the enzyme papain it has been noted that when these fibers are suspended in control solutions of NaCN at pH 7 certain of the fibers exhibit an instability similar to that of casein bristle, as shown in Figure 2. The marked disintegration of the peanut fiber, however, may be due to a reversible inactivation of the enzyme in a degree to which this fiber alone is susceptible.

Figure 3 represents the results obtained when the percentage digestion due to the enzyme alone is calculated; that is, the nonprotein nitrogen present due to exposure to the heat-inactivated preparation deducted from the total nonprotein nitrogen as recorded in Figure 1. It is clear that the digestion of the peanut fiber is most marked during the first week of exposure; the effect thereafter, as demonstrated in Figure 2, appears to be merely that of dissolving unless the assumption of the reversibility of inactivation of the enzyme is valid. Casein bristle shows rapid enzymatic degradation during the first week and thereafter gives the effect of resisting digestion. The activity of the enzyme in the later stage may be hindered by the accumulated end-products of digestion or by the presence of the hardening agents.

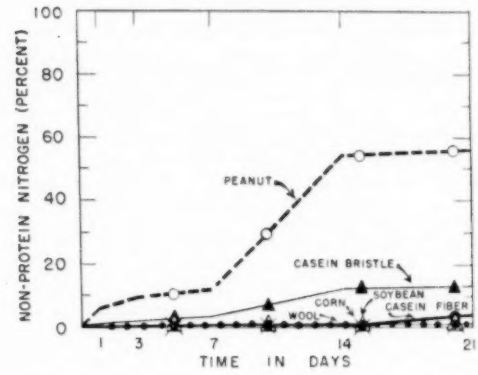

FIG. 2. *Percentage of the nitrogen in the fibers present at indicated time, due to exposure to heat-inactivated enzyme preparation.*

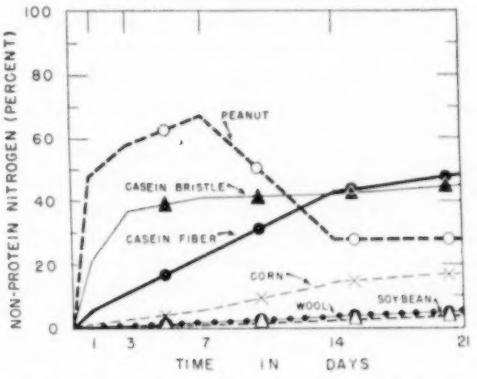

FIG. 3. *Percentage of the nitrogen in the fibers present as nonprotein at indicated time, due to action of enzyme alone (percentages of Figure 2 deducted from those in Figure 1).*

Casein fiber shows resistance to digestion in the early period of exposure, with continued susceptibility over the incubation period. The corn fiber gives a similar curve, with less total digestion. The curves for the casein and corn fibers demonstrate activity of the enzyme throughout the 3-week period, although there is a leveling-off tendency after the second week. Soybean and wool show a similarity in resistance to the enzyme, but soluble nitrogenous materials are detectable after the third week of exposure to the enzyme preparation. The resistance of soybean may be due to some substance in soybean similar to or identical with the antitrypsin factor [6].

Although the enzyme preparation was derived from cultures which had been incubated for 1 mo., there was no apparent disintegration of the mycelium, a condition which may be observed in a 2-mo.-old culture. The preparation may well be a mixture of intracellular and extracellular enzymes, since the almost complete digestion of the peanut fiber suggests peptidase activity, sometimes attributed to endoenzymes. No attempt was made to identify the end-products.

In some preliminary studies, it was noted that little detectable proteolytic activity was obtained from a 2-wk.-old culture. Furthermore, the enzyme appeared only after the organism established itself on the surface of the medium.

Summary

A method has been described for the preparation of a cell-free proteolytic enzyme elaborated by an actinomycete. The activity of the enzyme has been demonstrated on wool as well as on several fibers derived from proteins from milk, corn, peanuts, and soybean. The enzyme preparation was sufficiently active to digest to some extent all the protein fibers; soybean and wool showed the least susceptibility. With the exception of the soybean, it would appear that the stability of protein fibers to enzymatic digestion, imparted by the manufacturing processes, is not of the same order as that found in the protein of wool.

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Ion-Exchange Characteristics of Chemically Modified Cotton Fabrics

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SEVERAL chemically modified fabrics have been prepared recently which exhibit ion-exchange properties similar to those of the well-known granular ion-exchangers. These are produced by the introduction of a substituent group with basic or acidic properties into the cellulose molecule under such conditions that the fabric structure is retained.

Free amino groups may be introduced into the cellulose molecule by the process of Guthrie [2, 3] or that of Hartman [4]. The cellulose, thus chemically modified, is in reality an insoluble base and, therefore, is useful as an anion-exchanger. When the cellulose used is that of cotton fibers organized in a fabric the product offers an enormous surface for ion exchange. Such fabrics may be introduced and removed readily in carrying out a batch process such as the dispersion and precipitation of proteins [5].

Similarly, by introducing a substituent group with acidic properties into the cellulose molecule a cation-exchanger may be obtained. The use of fabrics of phosphorylated cotton, and the succinic acid half ester of cotton as cation-exchangers, has been suggested previously [5, 6, 7]. Partially carboxymethylated cotton has also been found to have cation-exchange properties. Timell [10] reported the preparation of sulfethoxycellulose. His product cannot be used as an ion-exchanger because its high degree of substitution makes it water-soluble. Under the conditions described below, however, a partially substituted sulfethoxycellulose fabric with good cation-exchange properties was prepared.

The application of a particular ion-exchanger to a particular use depends to a large extent on the pH range in which the exchanger is effective. This useful pH range is dependent on the acid or base strength of the exchanger. In order to evaluate and characterize the fabric ion-exchangers mentioned above and several others, the variation in their ion-exchange capacity as a function of pH was determined. Gregor and Bregman [1] have shown for the resinous cation-exchangers that in the presence of excess neutral salt the relation of capacity to pH is the equivalent of the titration curve of the acid groups. A similar relationship exists with respect to cellulosic cation- and anion-exchangers. If a cation-exchanger in the acid form (HA) is allowed to exchange with a neutral salt according to the reaction

$$HA + NaCl \rightleftharpoons NaA + HCl$$

an equilibrium is established. The acid released is equivalent to the salt form of the exchanger. The equilibrium is shifted to the right as the pH is increased until all of the exchanger has been converted to the salt form and the exchanger exhibits its maximum capacity. Consequently, the pH at which the exchanger exhibits half of its maximum capacity corresponds to the half-neutralization point of the exchanger and is a measure of the pK_a of the cation-exchanger. Similarly, the pH at which an anion-exchanger exhibits half of its maximum capacity is a measure of its base strength. The maximum capacity of a particular cellulosic ion-exchanger is a measure of the degree of substitution and varies with the conditions under which the fabric is chemically modified. The pH at half capacity, however, is a characteristic of the substituent group, and a measure of the acid or basic strength of the material.

Preparation of Modified Cotton Ion-Exchangers

Kier-boiled cotton sheeting was phosphorylated [6] by wetting it with a solution containing 49.6% urea, 18.4% phosphoric acid, and 32% water, squeezing out the excess solution, heating the fabric for 30 min. at 150°C, and washing thoroughly. It contained 4.6% phosphorus.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

The succinic acid half ester [7] of cellulose was prepared by heating cotton fabric with a 10% solution of succinic anhydride in dry pyridine at 60°C for 26 hrs. and washing thoroughly.

Partially carboxymethylated cellulose [8] was prepared by wetting cotton fabric with a 40% aqueous solution of monochloroacetic acid, squeezing out the excess, mercerizing by soaking for 1 hr. in 42% sodium hydroxide, and washing thoroughly.

Mercerized cotton fabric was wet with a solution containing 25% sodium hydroxide, 10% sodium β-chloroethyl sulfonate, and 65% water, and then heated for 45 min. at 100°C and washed thoroughly to produce sulfethoxycellulose. Cotton fabric treated in this way shows a high affinity for basic dyes, giving much darker shades than untreated fabric.

Aminoethyl cellulose [2, 3] for use as an anion-exchanger was prepared by wetting cotton fabric with a solution containing 25% sodium hydroxide, 10% 2-aminoethyl sulfuric acid, and 65% water, heating for 40 min. in a drying oven at 100°C, and washing thoroughly.

Diethyl aminoethyl cellulose [4] was prepared by wetting cotton fabric with a 10% aqueous solution of β-chloroethyldiethylamine, drying, and then mercerizing with a 25% solution of sodium hydroxide overnight at room temperature. The fabric was then thoroughly washed. A quaternary aminized cellulose was prepared by submerging diethyl aminoethyl cellulose in a boiling 10% solution of methyl iodide in absolute ethanol under reflux for 2 hrs.

The cation-exchangers, phosphorylated cellulose, the half ester of cellulose with succinic acid, carboxymethyl cellulose, and sulfethoxycellulose were each converted to the acid form by soaking in 5% hydrochloric acid for 20 min. The excess acid was removed by repeated washing with distilled water. The complete removal of excess acid was verified by the development of a pink color on addition of a drop of phenolphthalein indicator and a drop of 0.1*N* sodium hydroxide solution to 50 ml. of the wash water in which the exchanger had been soaked for ½ hr.

Both sulfethoxycellulose and phosphorylated cellulose when air-dried in the acid form gradually lose strength on storage. When stored in the salt form, however, no appreciable tendering has been noted.

The anion-exchangers, aminoethyl cellulose, diethyl aminoethyl cellulose, and quaternary aminized cellulose were converted to the basic form by treatment with 5% sodium hydroxide for 20 min. The excess alkali was removed by washing with successive portions of distilled water, allowing each portion to remain in contact with the anion-exchange fabric for several minutes. This washing was continued until the pH of the wash water was less than 6.0.

Aminoethyl cellulose and diethyl aminoethyl cellulose may also be regenerated by treatment with 5% ammonium hydroxide. The excess ammonia is readily removed by drying. Quaternary aminized cellulose is not regenerated to its full capacity by treatment with dilute ammonium hydroxide.

Evaluation of Capacity and Strength

After regeneration the fabrics were allowed to air-dry. They were then cut into small pieces (about 1 cm. square) and mixed thoroughly to obtain representative sampling. Samples of approximately 1 g. were weighed into glass-stoppered Erlenmeyer flasks. To each flask were added exactly 50 ml. of 1*M* sodium chloride solution, a suitable known amount of standard acid or alkali to produce the desired pH, and sufficient carbon-dioxide-free distilled water to make the total volume of liquid exactly 100 ml. For very low pH values a blank determination was run on a duplicate sample, omitting the sodium chloride. The flasks were allowed to stand, with occasional shaking, for 20 hrs. to equilibrate. The pH of the solution was determined with a glass electrode and an aliquot titrated to the phenolphthalein end-point to determine the capacity of the exchanger.

Moisture was determined by drying portions of the regenerated air-equilibrated materials in a vacuum oven at 60°C for 16 hrs. in order to calculate the capacities on a moisture-free basis.

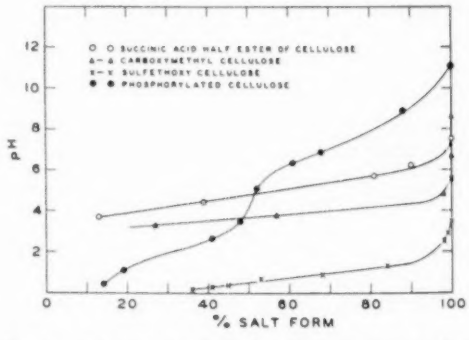

FIG. 1. *Relation of cation-exchange capacity to pH in chemically modified celluloses.*

TABLE I. MAXIMUM ION-EXCHANGE CAPACITY AND pH AT HALF CAPACITY OF SEVERAL CHEMICALLY MODIFIED COTTON FABRICS

Chemical modification	Maximum capacity (milli-equivalents per kg.) (dry basis)	pH at half capacity
Sulfethoxycellulose	340	0.5
Phosphorylated cellulose, 1st hydrogen	1280	1.5
Phosphorylated cellulose, 2nd hydrogen	2560	7.5
Carboxymethyl cellulose	248	3.65
Succinic acid half ester	247	4.75
Aminoethyl cellulose	600	8.0
Diethyl aminoethyl cellulose	246	7.7
Quaternary aminized cellulose	242	9.5

The capacities of the cation-exchange fabrics are plotted as a function of pH in Figure 1. In order to reduce these curves to a common basis the capacity has been calculated as the percent of the exchanger in the salt form. In agreement with other investigations [9], it is apparent that phosphorylated cellulose behaves like a dibasic acid and the characteristics of its ion-exchange capacity *vs.* pH curve are similar to those of the neutralization curve for the first two hydrogens of phosphoric acid. Sulfethoxycellulose exhibits the behavior of a strong acid, whereas carboxymethyl cellulose and the succinic acid half ester yield curves of the type characteristic of weaker acids. It is also apparent that all of these fabric exchangers except phosphorylated cellulose are unifunctional, a definite advantage for many purposes. The pH at which the exchanger has 50% of its maximum capacity may be used as an approximation of its pK_a. As shown in Table I, this value for the succinic acid half ester of cellulose (4.75) is of the same order as the pK_a for succinic acid (4.18) and the value for carboxymethyl cellulose (3.65) is near the pK_a for acetic acid (4.76).

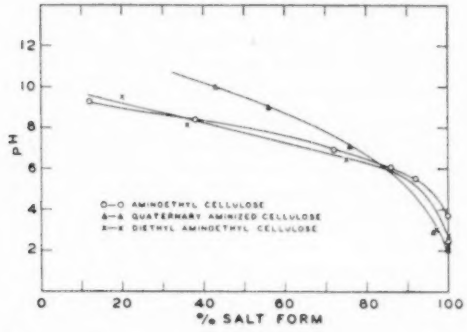

FIG. 2. *Relation of anion-exchange capacity to pH in chemically modified celluloses.*

The curves for the ion-exchange capacity *vs.* pH for the anion-exchange fabrics (Figure 2) indicate the base strength of these materials. Diethyl aminoethyl cellulose, a tertiary amine, is a slightly weaker base than aminoethyl cellulose, a primary amine. Quaternary aminized cellulose has the same maximum capacity as the diethyl aminoethyl cellulose from which it was made but is a much stronger base than the other anion-exchange fabrics.

In Table I are shown the maximum capacities and the pH's at half capacity for the cation- and anion-exchange fabrics investigated. These data and the curves in Figures 1 and 2 indicate that the acid and base strengths of these fabric ion-exchangers offer a selection comparable to that of commercial exchange resins. The maximum capacities reported are considerably below those of granular ion-exchangers, but for certain uses the advantage offered by the unique physical structure of the fabric ion-exchangers compensates for their lower capacity.

Summary

Several chemically modified cotton fabrics have been prepared and their characteristics as anion- and cation-exchangers have been evaluated. Phosphorylated cotton fabric behaves like a dibasic acid, with acid strength comparable to that of the first and second hydrogens of phosphoric acid. Partially sulfethoxylated cellulose is a strong-acid cation-exchanger, whereas carboxymethylated cellulose and the succinic acid half ester of cellulose are weakly acidic cation-exchangers. Aminoethyl cellulose, a primary amine, and diethyl aminoethyl cellulose, a tertiary amine, are weakly basic anion-exchangers. On treatment with methyl iodide, diethyl aminoethyl cellulose is converted to a quaternary compound which serves as an anion-exchanger of high basic strength.

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The Swelling of Cotton in Water: A Microscopical Study*

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Abstract

A method is described for comparing microscopically the cross-sectional areas of the same cotton fiber in wet and dry conditions, for evaluation of swelling. Results indicate the change in cross-sectional area of raw cotton fibers to be between 21% and 34% of the dry area regardless of variety of cotton or degree of maturity of the fiber. Immature samples show slightly less mean swelling than mature samples, but this is believed to be due to the presence of fibers with no secondary thickening at all which tend to shrink in cross-sectional area rather than swell. In the immature fibers deformation (defined as change in circularity) is slightly more than that of mature fibers. This, coupled with the fact that in a given weight of immature fibers there are approximately twice as many fibers as in a like weight of mature fibers, helps to explain the greater closing capacity of yarns made from immature cotton. Flax and a sample of viscose rayon show twice the swelling of cotton, Fortisan two-thirds as much, and nylon no cross-sectional swelling at all.

Introduction

It is common knowledge that there are differences in the swellability in water of fibers of different origins, especially as regards the greater swellability of flax and rayon over cotton. There are few data in the literature, however, on the extent of swelling, the changes in shape or dimensions of fibers, or the effect of fiber size and shape on swelling. Yet such information is basic to the utilization of fibers in a variety of uses such as for fillers in plastics, for warp yarns in carpets, and for industrial fabrics of all kinds where changes in dimension due to moisture are important in both processing and use.

In the improvement of water-resistant fabrics for military, agricultural, and apparel uses, design of the fabric is based on the fact that cellulose fibers swell on absorption of water and that such swelling helps in sealing the spaces in the fabric to offer a water-resistant material. Peirce, in developing the British Ventile fabric [11, 17], took advantage of the swellability of the cotton fiber by using the Oxford weave in the design of the fabric, but neither he nor others investigated the extent of cotton swelling. The present investigation was started in order to obtain a background of knowledge of the swelling of cotton

* Report of a study made under the Research and Marketing Act of 1946.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

A B

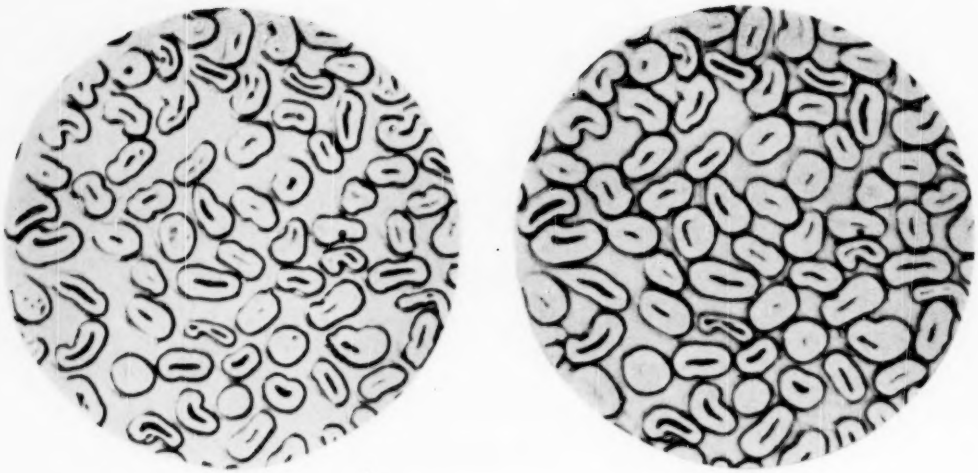
FIG. 1. *Cross sections of separated fractions of differentially dyed cotton. A—Thick-walled (mature) fibers (dyed red). B—Thin-walled (immature) fibers (dyed green).*

fibers in water-resistant cotton fabrics and to learn whether any varieties of cotton swell more than others and are more suitable for use in this type of fabric.

Up to the present the orifice test for yarn [16] has been the most useful guide to the utilization of the swelling properties of cotton. This test has shown repeatedly that yarns made from the less mature (thinner-walled) cottons have a better closing capacity than those made from mature (thick-walled) cottons; that fiber shape, closeness of packing, and size and shape of fiber interspaces probably contribute to this closing capacity; but that swelling also plays a part in closing capacity, as is demonstrated by using in the test a nonswelling liquid in comparison with water. For example, with the use of dioxane seepages were from four to twelve times as much as for water [16].

Since it was known from this work on the orifice test that yarns made from immature cottons retard the seepage of water better than those made from mature cottons, it was assumed in the beginning of the present work that the immature fibers probably swell more than the mature fibers. In the absence of data in the literature to support this view, and of other data on swelling of cotton fibers in water, the project was undertaken to investigate: (1) how much cotton swells in water; (2) whether immature fibers swell more than mature fibers of the same variety of cotton; (3) whether different varieties of cotton swell different amounts; and (4) whether fibers change shape upon swelling in water.

In consideration of these questions, the mechanism of the swelling of cotton as a fiber is of immediate importance. Cotton fibers are plant cells, each normal fiber consisting of a cellulose wall of appreciable thickness, with a very thin layer of cellulose of different structure on the outside, in which both pectin and wax occur as deposits; and with a central canal, or lumen, at the inside, where the protein-containing protoplasm manufactures the cellulose of which the fiber is composed. In the living condition the fiber is circular in cross section and the lumen is distended with protoplasm and plant fluids. By the time the boll has matured, however, and the cotton has been picked and ginned from the seed, the circular tube has collapsed and the fiber has shriveled into a flat and twisted ribbon. In many places along its length the lumen has been practically obliterated as a canal by the collapse of the fiber, while at other places it remains as a lenticular cavity for a short distance. The more mature the fiber, the smaller the lumen and the more nearly circular or elliptical the cross-sectional shape of the dried fiber, owing to the solid cellulose of which the wall is composed (Figure 1A). In immature fibers, on the other hand, the



A B

FIG. 2. *Swelling of thick-walled cotton fibers.* A—*Dry.* B—*Wet.*

cross-sectional shape of the shrunken cell is collapsed to a flat, rectangular contour which is often curved into a distorted "C" or "U" (Figure 1B). Sections in Figure 1 were made with a hand microtome [7].

Theoretical calculations by Skau [14] indicate that as the fiber swells in water a change in circularity is to be expected and that the thin-walled fibers would be expected to show (1) a greater percentage of swelling, (2) a higher degree of deformation, and (3) a higher rate of sorption because of the larger surface per unit volume. Again there were no experimental data to support these views.

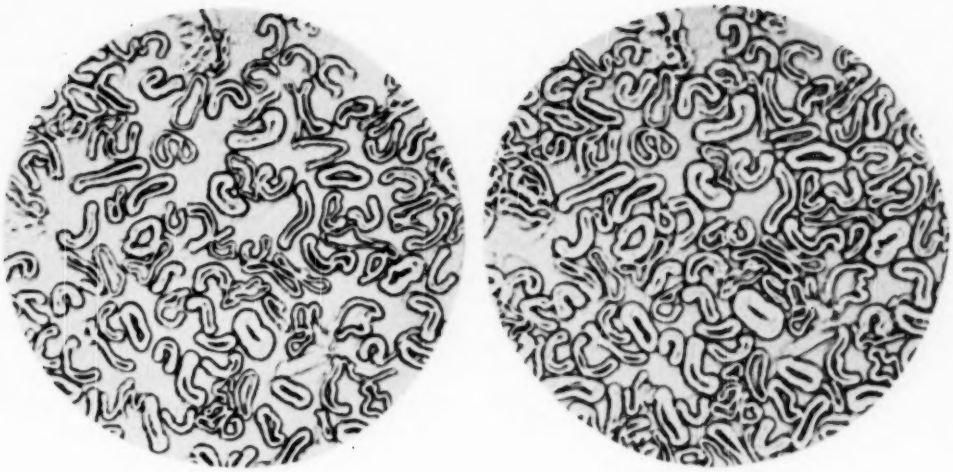
It has long been known that the increase in length of cotton fibers from the air-dry state to saturation in water is about 1%. Collins [2] states that in view of this negligible increase the change in length may be ignored, and that the swelling in fibers may be adequately indicated by changes in diameter. In discussing fundamental principles that govern the shrinkage of cotton goods caused by washing he shows [3] that the increase in diameter is comparatively large; from absolute dryness to water (saturation in water) there is approximately a 20% increase in diameter; and from an atmosphere of 45% relative humidity to water, about a 14% increase. Collins, however, was using cotton which had been swelled with 15.2% sodium hydroxide rather than raw cotton, and he measured fiber ribbon width rather than cross-sectional area.

In fact, most of the literature dealing with the swelling of raw cotton in water has been concerned with the swelling of cellulose in the alkali metal hydroxides or with the moisture responses of alkali-treated cotton [13]. A few investigators, however, report results on swelling in water. In 1905 von Höhnel [8] reported the swelling in water as "change in thickness" measured microscopically as the diameter of the cross section and showed the swelling of cotton to be 27.5%. In 1917 Haller [6] measured with an ocular micrometer the change in ribbon width of cotton fibers swelled with water and expressed the increase due to swelling as a percentage of the original width. He reported that air-dried cotton after immersion in water showed an increase in ribbon width of 16%, and that a similar fiber, air-dried and then desiccated over sulfuric acid for 4 days, showed a decrease in ribbon width of 5.5%. In 1947 Morehead [9], in describing a new technique for measuring the swelling changes in cross-sectional area of fibers, gave 21% for cotton and 47% for flax, from the air-dry state to saturation in water; but no details are given as to the origin or pretreatment of the cotton.

Materials and Methods

Samples

Cottons selected for these comparisons in the present investigation included: (1) Rowden, a coarse,



A B

FIG. 3. *Swelling of thin-walled cotton fibers.* A—*Dry.* B—*Wet.*

heavy-walled variety with a high orifice-test leakage; (2) Sea Island Special, an unusually coarse strain, with fibers almost as large as those of Rowden; (3) Empire, a normally developed Upland cotton of average diameter; and (4) Sea Island Seaberry, a representative of the fine-fibered cottons. In addition were included (5) Acala 1517 "Well-grown," of normal development, (6) Acala 1517 "Bollies," which was frost-damaged before the end of the maturing season and had an unusually high percentage of immature fibers. These two samples of Acala 1517 were grown on the same field but were harvested at different periods in the growing season.

Application of the differential dyeing technique [5] to these samples resulted in fibers of two colors which could be separated manually into two parallel samples for each of the 6 cottons tested: one in which the fibers had dyed green and were predominantly thin-walled and flat in cross-sectional shape; the other in which the fibers had dyed red and were thick-walled and more or less elliptical in cross section. The 12 samples were handled separately and planimeter measurements were made of cross sections of the fibers in the wet and dry states.

For comparative evaluation of the microscopical procedures employed, samples of viscose staple fiber,* nylon,† Fortisan,‡ and raw flax § were also measured for increase in cross-sectional area on wetting.

Procedure

Small bundles (approximately 15 mg.) of fibers, combed parallel and held under slight tension (1 lb.) in a Chandler bundle device [12], were wrapped securely at either end, leaving a free region at the center section unwrapped for approximately $\frac{1}{4}$ in. The relaxed bundle was then immersed in water containing a wetting agent (0.5% Aerosol OT) for 20 hrs. to insure maximum swelling of the fibers.

The soaking-wet bundle, held vertical by means of very slight tension (less than 1 lb.) just sufficient to hold the fibers parallel in the bundle, was immersed in methyl methacrylate solution containing a plasticizer and a catalyst and polymerized at 58°C for 15 hrs. The following proportions gave the best consistency for sectioning with a rotary microtome: 0.25 g. benzoyl peroxide; 50 ml. methyl methacrylate monomer; 17 ml. Santicizer M-17 (methyl phthalyl ethyl glycollate).

The cross sections were cut on a rotary microtome at a thickness of 8μ to 10μ and attached to the slide

* Avisco 1.5 den., 5 in.

† Nylon 210-69-1-Z, bright yarn, unsized and unoiled.

‡ Fortisan 1,100 den., 1,440 filament, 2.52 twist, special high tenacity.

§ Raw flax, hackled and combed.

with a peanut protein adhesive. The polymeric methacrylate embedding material was removed by rinsing the slide repeatedly in methacrylate monomer. The slide was then immediately immersed in water containing a wetting agent for approximately 2 min., and the section mounted in water under a coverslip and photographed at a magnification of 500 × (Figures 2B and 3B). (In order to adjust the refractive index for better contrast in photography, a trace of glycerin was added to the water just before photographing.) The uncovered slide was then immersed in an acetone bath for 2 hrs., dried by evaporation, and placed in a desiccator over phosphorus pentoxide (P_2O_5) for approximately 20 hrs. Mounted in cineole,* the fibers were photographed in the dry state at a magnification of 500 × (Figures 2A and 3A). The final prints were enlarged photographically to 1,125 × and areas of individual fibers were measured with a planimeter. Swelling was calculated on the basis of change in dimensions from the wet to the dry state:

$$\frac{\text{Wet area} - \text{dry area}}{\text{Dry area}} \times 100 = \% \text{ swelling.}$$

Comparison of Swelling of a Thin Section of a Fiber with That of the Whole Fiber

Because considerable technical difficulty was experienced in keeping the cotton fiber sections upright on the slide, especially when they were wet with water, in the procedure adopted as standard the fibers were first wet, then embedded, sectioned, and photographed in the wet condition, being subsequently dried and rephotographed in the section form. In the few experiments which were attempted on the successive wetting and drying of fibers, rewetting of the slide resulted in almost every case in the loss of more than half of the specimens, so that cross-sectional pictures could not be obtained on more than a few fibers at a time.

Moreover, in the standard procedure it was hoped that by wetting the entire fiber before sectioning any osmotic forces at work in the whole fiber would be effective to produce maximum swelling. However, some question was raised as to whether maximum swelling was actually attained. Accordingly, fibers embedded wet in methyl methacrylate were compared for swelling with those embedded dry and subsequently soaked in water with a wetting agent for 3 hrs.

Treatment	*Mean swelling, %*	*No. fibers*
Mature fibers, embedded wet, then dried	34.1	500
Mature fibers, embedded dry, then wetted	32.5	90

No significant differences are apparent as to the amount of swelling measured in the two methods of embedding.

Studies of Drying Methods

In view of the evidence [18, 19] that removal of water from cellulose by means of solvents leaves the cellulose in a more reactive and presumably a more porous state, it appeared that the predrying by rinsing in acetone before desiccation over P_2O_5, as practiced in the standard technique, might leave the fibers in a distended condition even after desiccation and thus produce a false impression of the small change in area which occurs on going from the wet to the dry state. To investigate this phenomenon, fibers were compared for change in area when dried under different conditions.

Treatment of fibers (after photographing wet)	*Mean swelling, %*	*No. fibers*
(*a*) Dried by standard acetone-rinsed, P_2O_5 desiccation method	34.1	500
(*b*) Dried in an oven for 1 hr. at 110° C	27.7	200
(*c*) Dried from state of saturation over P_2O_5 (168 hrs.)	22.9	200
(*d*) (*c*) dried over P_2O_5 (336 hrs. total)	23.8	200
(*e*) (*c*) and (*d*) dried over P_2O_5 (1,062 hrs., total)	27.8	200
(*f*) (*c*), (*d*), and (*e*) dried by standard acetone-rinsed method (desiccated over P_2O_5 20 hrs.)	33.9	200

Obviously, predrying in acetone before desiccation in P_2O_5 does not measurably reduce the final change in area of the fiber but would appear, rather, to reduce the restrictive effect of hornification in the drying of the fiber.

After thoroughly drying, the same cross sections as in (*c*) to (*f*) were rewet by soaking in water for 1 hr., photographed in water, dried by the standard acetone-rinsed method, and desiccated over P_2O_5 for 20 hrs. The mean difference in cross-sectional area between the dry and the saturated state was 33.22%.

* Moisture analysis of cineole (Karl Fischer method) gave 0.25%.

calculated individually for each of the 196 fibers which survived the immersion. This percentage swelling and the value for (f), 33.9%, are in excellent agreement with the value for (a), 34.1%, determined independently some 10 months previously.

Investigation of Cell Wall Exclusive of Lumen

In the majority of fiber cross sections the lumen is so collapsed that it is not possible with the planimeter to make accurate measurements of its area. For this reason swelling was calculated as the over-all change in area of the whole cross section (based on planimeter measurements around the outside perimeter of the fiber) without regard to the lumen. Since in the case of yarns and fabrics it is the closure of spaces between fibers that contributes to water resistance, the increase in over-all size of the fiber is the factor of prime interest in a study of the swelling of cotton.

Nevertheless, in order to explore briefly the swelling of the cellulose of the fiber wall the lumens were measured in 50 selected fibers in which the opening was large enough to be readily traced with the planimeter. As would be expected, swelling of the cellulose was in every case somewhat greater than the increase in area calculated for the whole fiber; and in mature fibers this difference was much less than in immature fibers. The results follow:

Sample	*Change in area of cross section mean, %*	*Change in area of cell wall mean, %*
Empire Bale 92, mature fraction	35.5	37.8
Empire Bale 92, immature fraction	16.7	29.9
Rowden, mature fraction	25.6	28.8
Rowden, immature fraction	33.4	49.2

Too much significance should not be attached to the absolute values because in any given sample of cotton only a small percentage of fibers have lumen openings large enough to measure, and because the accuracy of planimeter measurements of extremely small areas is limited. Suffice it to say that the actual swelling of the cellulose wall in the fiber is somewhat greater than the increase in area of the whole fiber cross section.

Changes in Fiber Shape on Swelling

It had been theorized [14] that the immature fibers would return to circularity upon swelling. To investigate this theory, deformation of the fibers was studied by determining the change in circularity of the cross section of the individual fiber from saturation to the dry condition. Circularity is here defined [15] as a relationship between perimeter (P) and area (A) such that

$$\frac{4\pi A}{P^2} = 1 \text{ for a true circle.}$$

The perimeter of individual fibers was measured with a device developed at the Southern Regional Research Laboratory [10] for measuring linear distances. The relationship of perimeter and area was determined for individual fibers in both mature and immature portions of each sample. Maximum circularity for mature fibers was found to be approximately 0.93 and minimum circularity for immature fibers approximately 0.15. The change in shape of each fiber from the wet to the dry state was expressed as a percentage of the circularity in the dry state.

Results

Swelling

The mean swelling for both mature and immature fractions of the 6 cotton samples is given in Table I, together with the swelling values for the other fibers, which were measured for comparison.

Figure 4, which shows the frequency distribution for swelling of a typical cotton sample, indicates that the measurements show normal distribution for both mature and immature fractions of the sample and that, as would be expected, dispersion is greater in the underdeveloped than in the mature fibers. Data for the other samples studied yielded similar normal curves.

The difference in swelling between cotton and other cellulose fibers is impressive. Differences in amount of swelling between different varieties of cotton are less pronounced, and too small to be of practical significance. The differences between mature and immature fractions, while statistically significant, are not sufficient to explain the considerable differences in closing capacity observed in leakages in the orifice test [16]. The conflicting data on microscopical and orifice tests seem to indicate that in the closing capacity of a cotton in yarn or fabric surface area and distribution of fiber interspaces are more significant than swelling.

The result reported for nylon is taken as an ex-

TABLE I. CROSS-SECTIONAL SWELLING* OF INDIVIDUAL FIBERS (CHANGE IN AREA FROM WET TO DRY STATE)

	No. fibers	Dry area mean (μ^2)	Change in area* mean (%)	Standard error of mean	Significance (1% level) of difference in mean % change in area between mature and immature fibers
Cotton					
Rowden, mature	1,400	203.0	26.16	0.25	Very significant
Rowden, immature	1,400	96.4	30.57	0.45	
Sea Island, Special, mature	500	191.2	33.27	0.48	Significant
Sea Island, Special, immature	500	82.2	29.32	0.90	
Empire, bale 92, mature	1,100	157.9	31.72	0.35	Very significant
Empire, bale 92, immature	1,100	92.4	20.83	0.52	
Acala, "Well-grown," mature	600	129.5	26.59	0.42	Barely significant
Acala, "Well-grown," immature	600	75.8	28.79	0.78	
Acala, "Bollies," mature	525	122.4	33.54	0.47	Significant
Acala, "Bollies," immature	525	74.3	30.61	0.77	
Sea Island, Seaberry, mature	500	121.6	34.11	0.45	Very significant
Sea Island, Seaberry, immature	500	71.1	27.06	0.91	
Comparative fibers					
Flax, raw	100	150.9	64.9	1.68	
Viscose rayon, staple	100	112.2	66.2	1.34	
Fortisan	150	61.6	19.9	1.54	
Nylon	300	318.3	−1.88	0.19	

* $\frac{\text{Area wet} - \text{Area dry}}{\text{Area dry}} \times 100 = \%$ swelling.

TABLE II. CHANGE IN CIRCULARITY* OF INDIVIDUAL FIBERS ON SWELLING IN WATER

Fibers	Average dry circularity*	Change in circularity* mean (%)	No. fibers	Standard error
Rowden, mature	0.75	5.4	100	1.49
Rowden, immature	0.40	6.6	100	1.18
Sea Island, Special, mature	0.79	3.5	100	0.52
Sea Island, Special, immature	0.48	10.1	100	1.66
Empire, mature	0.71	6.4	100	0.81
Empire, immature	0.34	4.0	100	1.35
Acala, "Well-grown," mature	0.75	3.1	100	1.20
Acala, "Well-grown," immature	0.40	10.1	100	1.95
Acala, "Bollies," mature	0.70	5.5	100	1.23
Acala, "Bollies," immature	0.39	10.2	100	1.91
Sea Island, Seaberry, mature	0.75	6.9	100	0.90
Sea Island, Seaberry, immature	0.40	7.2	100	1.42

* Circularity $= \frac{4 \pi A}{p^2}$. Circularity for a true circle = 1. Maximum circularity found for mature fibers was 0.93; minimum circularity for immature fibers, about 0.15.

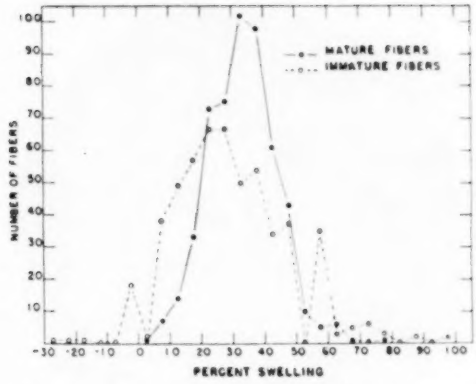


FIG. 4. *Frequency distribution for change in area of fibers of a typical cotton sample from dry state to saturation in water.*

pression of experimental error in the method.* Because the refractive index of this fiber is so near that of the mounting medium used, it was extremely difficult to obtain a sharp enough focus on the fibers for photographing; and reproducibility of planimeter measurements is between 1% and 2%.

It is to be noted that the swelling of the raw flax and the viscose rayon under consideration here was almost exactly twice that of cotton. These data are in line with the relationship indicated by Morehead's measurements [9].

Changes in Fiber Shape on Swelling

Average circularity measurements for 100 fibers of each type of cotton considered in these studies are

* "Water, glycerin, and a 10% sodium hydroxide solution at room temperature cause no lateral swelling of nylon fibers. Boiling with 10% Glauber's salt causes a 3% swelling" [4].

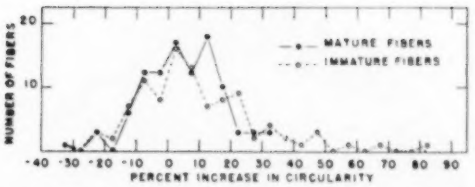


FIG. 5. *Frequency distribution for change in circularity of fibers of a typical sample of cotton from dry state to saturation in water.*

shown in Table II. While the fibers did tend to become more circular as they swelled, the change in shape was less than might have been expected in fibers which are relatively free from external restrictions. It is apparent that the immature fibers showed a trend toward greater change in shape upon wetting than the mature fibers. Figure 5 shows a normal frequency distribution for circularity measurements in both types of fibers.

Discussion

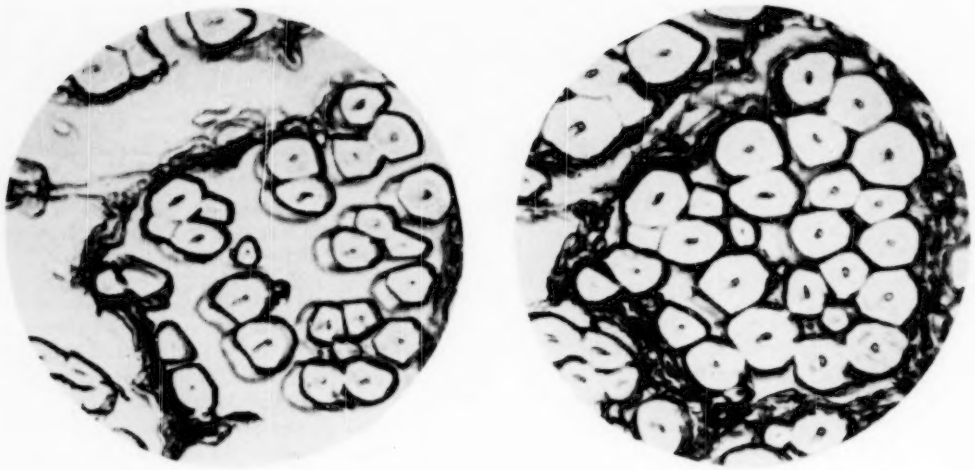
A chief cause of the many variations in the results on cross-sectional swelling of cotton may lie in the extreme natural variation in cotton fibers and the impossibility of uniform sampling.

TABLE III. SWELLING OF EMPIRE COTTON SAMPLES

Sample	No. fibers	Change in area mean (%)	Standard error of mean
Bale 92, mature	1,100	31.7	0.58
Bale 92, immature	1,100	20.8	0.52
Bale 99, mature	500	22.8	0.50
Bale 99, immature	500	25.7	0.72
Florence, S. C., mature	900	25.7	0.32
Florence, S. C., immature	900	20.5	0.53

TABLE IV. SWELLING OF COTTON FIBERS (CORRECTED BY OMISSION OF ALL NONSWELLING FIBERS)

Variety of cotton	Immature			Mature
	Mean swelling (%)	Nonswelling fibers (%)	Corrected mean swelling (%)	Mean swelling (%)
Empire, bale 92	20.8	16.4	25.6	31.7
Empire, bale 99	25.7	6.6	27.6	22.8
Empire, Florence, S. C.	20.5	12.1	23.6	25.7
Sea Island, Seaberry	27.1	13.8	32.0	34.0
Acala, "Well-grown"	28.8	8.7	31.7	26.6
Acala, "Bollies"	30.6	3.8	32.0	33.5
Sea Island, Special	29.3	8.8	32.3	33.3
Rowden	30.6	4.0	31.9	26.2



A B

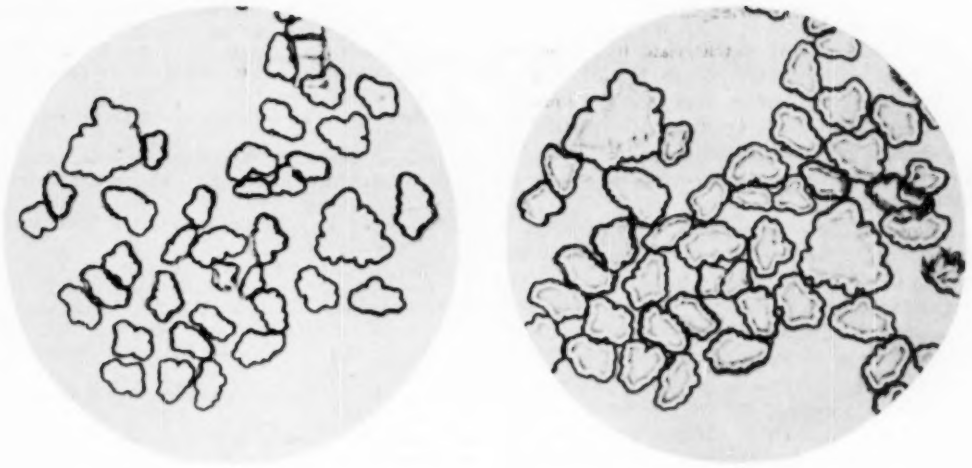
FIG. 6. *Swelling of raw flax fibers.* A—*Dry.* B—*Wet.*

The value for the swelling of the immature Empire fibers listed in Table I was considerably less than that for any of the other varieties measured. To investigate this anomaly, and to determine whether or not it might be a varietal characteristic, two additional samples of Empire cotton were measured. The results on the whole series of Empire samples are shown in Table III. The average mean swelling of immature Empire samples is 22% and of mature 27%; this variation and the low swelling of the Empire samples may be explainable on the basis of growth environment.

In a re-examination of the data it was found that in the immature fraction of each sample there is a fairly large percentage of fiber cross sections which show no swelling at all; many of these show shrinkage in over-all area rather than swelling. These are the sections of extremely thin-walled fibers with seemingly no cellulose thickening. Their nonswelling is explained by the fact that the cellulose fibrils of which the primary wall is composed are at an angle nearly perpendicular to the fiber axis, so that any swelling in fibers which have no secondary-wall development is largely in a direction parallel to the longitudinal axis of the fibers. This is confirmed in the literature by the work of Berkley [1], who found 25% increase in length for green fibers which were rewetted after drying from a 10-day-old boll. If all the fibers which show no cross-sectional swelling are removed from consideration in the data on Empire cotton samples, discrepancies in degree of swelling between mature and immature fractions become smaller. Data on all the cotton samples were again re-examined without taking into account nonswelling fibers. In the mature fractions all fibers showed some swelling, whereas in the immature fractions there were always a few fibers which showed no swelling and in some samples the percentage was relatively large. Swelling percentages re-evaluated in this way for all sets of data are shown in Table IV.

Changes in Fiber Shape on Swelling

It is obvious from Figures 2 and 3 that there is little visible change in shape of any particular cotton fiber upon swelling in water. In Figures 6 and 7, where extent of swelling is more readily apparent in a visual comparison of the dry and wet fibers of flax and rayon, there is also little evidence of change in fiber shape. It was observed that while swelling seems to entail only a simple enlargement of the whole fiber, there is in cotton often a greater change in the long diameter of the cross section than in the short diameter. This would imply that in cotton fibers "swelling" in water sometimes is more a matter of unwrinkling of the shriveled cell than a distention of the cellulose as such. Deformation of the fibers, especially those of little cell-wall thickness,



A B

FIG. 7. *Swelling of viscose rayon fibers.* A—*Dry.* B—*Wet.*

would contribute to the redistribution of the interspaces between fibers as they push one against the other during swelling. This effect would help to explain the superior closing capacity of immature over mature cottons.

Conclusions

In consideration of the questions posed in the Introduction to this report it may be said that these measurements of cross sections of fibers show:

1. That cotton swells from 21% to 34%, with an average of about 30%, whereas nylon does not swell; Fortisan swells about two-thirds as much as cotton; and flax and the particular sample of viscose rayon used in this investigation swelled about twice as much as cotton.

2. That differences between mature and immature fibers as regards increase in cross-sectional area in water, although statistically significant in the results reported, are small and inconsistent.

3. That differences in swelling between the varieties of cotton studied are slight, there being a maximum of 8% for mature fractions and of 10% for immature fractions.

4. That change in circularity of cotton fibers upon swelling in water was in no case more than 10%; and, while it seems possible that varieties differ somewhat, there is a slight tendency for the immature fibers to show more deformation than the mature fibers.

5. That the swelling of the fiber cell wall alone may be considerably greater than the swelling of the fiber as a whole. This might imply that the "swelling" of fibers as here reported may be due as much to the unfolding of the crumpled fiber tube as to the distention of the cell-wall cellulose.

The results of these studies imply that in the selection of cotton for the manufacture of water-resistant fabrics varietal differences with respect to swellability of fiber play little part. While mature and immature fibers swell about the same amount, the tendency is toward greater swelling for the mature fibers rather than for the immature fibers, but this result is probably due to the influence of nonswelling fibers found frequently in the immature fraction and seldom in the mature fraction of any sample of cotton. Since in a given weight of immature cotton there are from two to three times as many fibers as in a like weight of mature cotton, fiber interspaces are finer, and therefore the closing capacity of cottons of low maturity may be expected to be considerably greater than the closing capacity of normally mature cotton. These data corroborate earlier evidence on yarns and fabrics that cottons previously considered inferior because of a high percentage of thin-walled fibers may find a specialized use in the manufacture of self-sealing fabrics.

Acknowledgment

The use of methyl methacrylate for embedding wet fibers was suggested to us by Mr. Stanley Backer during cooperative work with the Philadelphia Depot of the Army Quartermaster Corps. We understand that the method originated with Mr. Henry Broadfoot, Massachusetts Institute of Technology.

Acknowledgment is given to many members of the staff of the Southern Regional Research Laboratory to whom we are indebted for assistance on this project, and especially to Mr. H. O. Smith and Miss Florence T. Roberts for dyeing the samples of cotton. Thanks are due to Mr. C. H. Billett of the Photographic Section for making the enlargements of our innumerable negatives; and we wish to express our indebtedness also to Dr. E. L. Skau, Mr. C. F. Goldthwait, Miss Geraldine M. Couturier, and Dr. Kyle Ward, Jr., for their helpful advice and counsel.

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Specific Volume of Native Cellulose

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Abstract

Specific-volume measurements of native cellulose determined in different media and calculated from x-ray data are compared. Data for the specific volume of cellulose containing different amounts of water measured in a benzene medium are analyzed. On the assumption that the difference between the specific volumes measured in benzene and the specific volume calculated from x-ray data is due to voids, and that the differences between the x-ray value and the values determined in water are due to the compacting of water, reasonable compression values are obtained that are in accord with the concept of hydrogen bonding of water and other findings.

CONSIDERABLE DIFFERENCE of opinion still exists regarding the interpretation of data for the specific volume of cellulose determined in various media. The whole difficulty centers around the fact that different displacement media used to measure the volume give different values owing to differences in accessibility of the cellulose to the fluid or the tendency for the fluid to become packed within the cellulose structure.

These difficulties can, for most purposes, be avoided by using the specific-volume value calculated from x-ray crystal-structure data that does not involve displacement measurements. This value is, unfortunately, not as exactly known as is desirable. Slight variations in the x-ray data used and in the value for the Avogadro number give calculated specific-volume values for native cellulose varying from 0.627 to 0.632 [9, 10]. Hermans [6, 8] gives an intermediate value of 0.629, which will be used in this paper.

A knowledge of the reasons why the different displacement media give different values for the specific volume is of considerable theoretical importance, even though the value obtained from x-ray measurements is accepted as the true value. Displacement data and their interpretation are of importance in permeability studies, in the determination of the degree of crystallinity of cellulose, and in the determination of the extent to which such polar liquids as water are packed in cellulose as a result of hydrogen bonding.

A brief review of the differences in the specific-volume values obtained in different media will be given, with reasons for the differences; and this review will be followed by data that support the thesis that values determined in water are low primarily because of a reduced volume resulting from hydrogen bonding.

Water gives the lowest and most consistent specific-volume values, with those for native cellulose ranging from 0.621 to 0.624 [4–7, 11, 13, 14]. The extent of cutting of the fibers seems to have a negligible effect upon the accessibility to water. Cotton linters and whole-fiber cotton give practically identical specific-volume values [13]. This is not surprising, as water opens up the structure as a result of swelling and makes voids accessible that would otherwise be inaccessible.

Nonswelling liquids give higher and more variable specific-volume values. Benzene, toluene, and carbon tetrachloride, which have similar molecular sizes, give quite similar values for any one cellulose [4, 6, 8, 16]. In the case of various native cottons, the values range from 0.637 to 0.650 [4, 8, 15, 16]. The form of the cellulose and the degree of crystallinity affect the values appreciably. Wakeham [16] has recently shown that cutting cotton fibers increases the accessibility to benzene and as a result decreases the specific-volume values. He has also shown that larger molecules, such as dioctyl phthalate, do not penetrate the voids so well as benzene and hence give still higher specific-volume values than benzene does. He believes that benzene measures the volume of the fibers, including the lumen in the case of whole fibers and the fiber walls in the case of cut fibers. This conclusion is not surprising, as traces of remaining adsorbed air in the extremely fine communicating structure could prevent the lumen of

* Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

the fibers from filling in the case of whole fibers, as very high pressures are needed to overcome surface-tension effects in fine capillaries. When the fibers are cut, no such resistance to filling exists.

Helium displacement gives intermediate specific-volume values between those obtained in water and those obtained in nonswelling liquids. Davidson [4] obtained values of 0.638 to 0.642 for different soda-boiled native cottons. Filby and Maass [5] obtained a value of 0.640 for standard cotton, and Walker * obtained a value of 0.634. Hansen and the present author [14] obtained a value of 0.631 for soda-boiled cotton-linter *alpha*-cellulose (99.3% *alpha*) at 30°C.† In the latter experiments, the fibers were cut. This cutting, combined with the fact that several hours were allowed for penetration equilibrium to take place, may account for the fact that this value was lower than those obtained by the other workers. That this value closely approaches the values calculated from x-ray crystal-structure data is interesting and indicates that not only microscopically visible voids but also any voids approaching molecular dimensions in the noncrystalline regions of the cellulose must be penetrated. This penetration is to be expected, since helium, next to hydrogen, is the smallest molecule known. Being a gas, it can diffuse through the finest capillaries, even though they may contain traces of residual air, without having to overcome the effect of surface tension.

Davidson [4] has shown that helium is not selectively adsorbed by cellulose. There is, furthermore, no evidence to show that helium swells cellulose. For these reasons, it is hard to conceive that helium forms a solid solution with cellulose, as postulated by Hermans [8]. To form a solid solution, it would have to create the space that it occupies by overcoming the cohesion of the cellulose structure. The lack of sufficient attractive force to cause adsorption, the author feels, is sufficient evidence to show that the take-up of helium is in existing capillaries and voids.

The take-up of water, on the other hand, can be visualized as the forming of a solid solution. If the concept of capillary permeability is to be used, the capillaries must be pictured as transient capillaries [13]. Under either concept there is sufficient evidence to show that water is selectively adsorbed by forces that considerably exceed the force of attraction of water for itself [13, 14]. Such forces could readily compact the water, as will be shown later.

Hermans [8] believes that in the process of forming a solid solution in cellulose, water enters voids in the noncrystalline areas rather than being compacted. In order for this to be true, water molecules must not only enter voids larger than their molecular dimensions but they must also approach the available hydroxyl groups of the noncrystalline regions more closely than the interplane distances in the crystal lattice of the crystallites in order to account for the fact that the specific-volume values are lower than the values for the crystallites obtained from x-ray data. The author believes that such proximity can be attained only as a result of appreciable molecular forces, and that these forces are satisfied by electron displacement and hydrogen bonding and probably by orientation which permits closer packing.

The filling of mechanical voids larger than molecular dimensions, on the other hand, can in a large measure be mechanical. The volume represented by the difference between the specific volumes of cellulose obtained in benzene and by x-ray measurements can be, and very probably is, to a high degree mechanically filled with water. This volume becomes almost completely filled with helium, and even with benzene when the latter replaces a swelling solvent, as has been shown by Soley.* Soley replaced the water in swollen cotton by alcohol, then replaced the alcohol by benzene, and finally determined the specific volume of the cotton in benzene. He found that the cotton retained 2% of water and corrected for its presence by using its normal specific gravity. In this way he obtained a specific-volume value of 0.630. On the basis of the water having been compressed, as in curves D and F of Figure 3, which will be described later, the specific-volume values for water-free cellulose would have been 0.631 and 0.633, respectively, for curves D and F. All three of these values indicate that the penetration of the cellulose by the benzene under such replacement conditions is similar to that of helium and that the specific volume of cellulose obtained in benzene approaches that determined by x-ray measurements.

Compacting of Adsorbed Water in Cellulose

In order to gain a better understanding of conditions under which penetration occurs and of the ex-

* Walker, F., Ph.D. Thesis, Department of Chemistry, McGill University, Montreal, Canada (1937).

† From coefficient of thermal expansion data [17] it is estimated that at 20°C the value would be 0.630.

* Soley, R. C., Ph.D. Thesis, Department of Chemistry, McGill University, Montreal, Canada (1940).

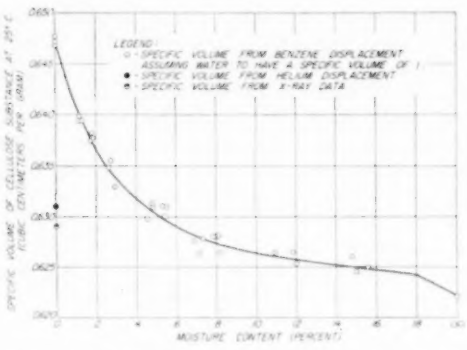
LEGEND:
○ - SPECIFIC VOLUME FROM BENZENE DISPLACEMENT ASSUMING WATER TO HAVE A SPECIFIC VOLUME OF 1
● - SPECIFIC VOLUME FROM HELIUM DISPLACEMENT
⊕ - SPECIFIC VOLUME FROM X-RAY DATA
SPECIFIC VOLUME OF CELLULOSE SUBSTANCE AT 25° C. (CUBIC CENTIMETERS PER GRAM)
MOISTURE CONTENT (PERCENT)

FIG. 1. *Relationship between moisture content and specific volume of native cellulose substance measured in benzene.*

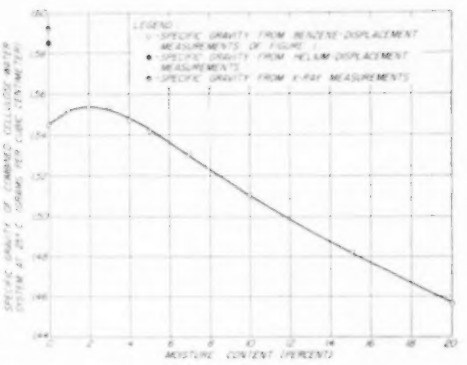
LEGEND:
○ - SPECIFIC GRAVITY FROM BENZENE DISPLACEMENT MEASUREMENTS OF FIGURE 1
● - SPECIFIC GRAVITY FROM HELIUM DISPLACEMENT MEASUREMENTS
⊕ - SPECIFIC GRAVITY FROM X-RAY MEASUREMENTS
SPECIFIC GRAVITY OF COMBINED CELLULOSE-WATER SYSTEM AT 25° C. (GRAMS PER CUBIC CENTIMETER)
MOISTURE CONTENT (PERCENT)

FIG. 2. *Relationship between moisture content and specific gravity of the combined native cellulose substance-water system. Specific gravity of system calculated on the basis that benzene measures the specific volume of cellulose substance and that water has its normal bulk density.*

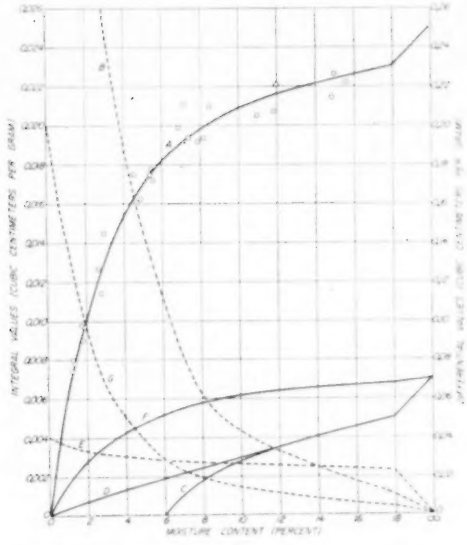
INTEGRAL VALUES (CUBIC CENTIMETERS PER GRAM)
DIFFERENTIAL VALUES (CUBIC CENTIMETERS PER GRAM)
MOISTURE CONTENT (PERCENT)

FIG. 3. *Relationship between compression of water and moisture content of cellulose substance. Solid curves A and C are integral curves based on the specific gravities of native cellulose determined in benzene and by x-ray measurements, respectively, with no unfilled voids present. Solid curve F is an integral curve based on the specific gravity of native cellulose from x-ray data, with all voids filled with water only above the fiber saturation point. Curve D corrects curve C for the case of unfilled voids below 12% moisture content. Curves B, E, and G are differential curves obtained from curves A, D, and F, respectively.*

tent to which compacting of adsorbed water can occur, the author has reanalyzed the data of Stamm and Seborg [15] for the specific gravity of native-cotton-linter *alpha*-cellulose containing different amounts of water measured in a benzene medium at 25°C. Figure 1 shows the relationship between the moisture content and the specific volume of cellulose V_a, calculated from benzene-displacement measurements by means of the following equation:

$$V_a = \frac{\dfrac{W_b - (W - m_1)}{d_b} - \dfrac{m_1 - m_o}{d_w}}{m_o}, \qquad (1)$$

On the basis of water having its normal density (d_w) m_o is the oven-dry weight of the cellulose, m is the wet weight of the cellulose, d_b is the density of benzene. W'_b is the weight of the pycnometer filled with benzene only, and W is the weight of the pycnometer filled with the wet cellulose and benzene. Figure 2 shows the relationship between moisture content and the specific gravity of the combined cellulose-water system, calculated from Figure 1 on the basis of water having its normal specific gravity. The curve is practically identical with that of Hermans [6, 8].

Hermans [6, 8] calculated the apparent density of adsorbed water at different moisture contents by using data similar to those in Figure 2. He plotted his results in such a way as to imply that the density of the adsorbed water had the constant value of 1.6 between 0% to 4% moisture content, and decreased

in value to 1.0 at the fiber saturation point. The present author feels that Hermans was not justified in plotting his differential curve in this way. The maximum in Figure 2 is not due to an abrupt change in the rate of change of the apparent density of water. The maximum occurs when the slow increase in apparent specific gravity of cellulose that occurs with penetration of the structure by water is overbalanced by the more pronounced decrease brought about by including the specific gravity of the contained water with the apparent specific gravity of cellulose. The error in Hermans' plot can be shown by calculating the apparent compression of water from the data used to obtain Figures 1 and 2, by means of the following equation:

$$C = \frac{m_1 - m_a}{d_a} - \left(\frac{W_b - (W - m_1)}{d_b} - \frac{m_a}{D}\right)^* \quad (2)$$

in which C is the apparent compression of the water in cc. per g. of cellulose, D is the assumed specific gravity of cellulose substance, and the other symbols have the same significance as in equation (1).

If it be assumed, as by Hermans [6, 8], that the nonswelling liquid benzene gives the true specific volume of cellulose substance (which implies that the cellulose substance contains no voids impermeable to benzene), the integral compression (curve A of Figure 3) can be calculated from the data used in obtaining Figure 1. Curve B was obtained by differentiating curve A. The apparent compression of the initially adsorbed water under these conditions is 0.7 cc. per g., and the apparent density of the water is 3.33 g. per cc. Hermans [6–8] and others who have opposed the adsorption-compression theory are certainly justified in doing so on the basis of such a value. The data, however, may be analyzed differently with quite different results. Before this is done, however, it should be pointed out that curve A is a smooth curve with no inflections. It is inconceivable that a zone of constant compression could occur between a moisture content of 0% and 4% on the basis of this and of thermodynamic data [13].

If the specific gravity of cellulose calculated from x-ray data rather than the value determined in benzene be used in equation (2), curve C will be obtained in place of curve A. It should be noted that the difference between the two curves is an additive constant volume per unit weight, since only D in equation (2) is shifted by a fixed amount. Use of a larger value for the specific gravity of cellulose than that obtained in benzene implies that cellulose substance contains voids impermeable to benzene. If curve C be drawn parallel to curve A, it will be further implied that these voids are completely filled with water at all values of the moisture content of cellulose. This condition cannot exist at low moisture contents. Hence, curve C cannot be parallel to curve A down to a zero moisture content. In fact, it cannot be parallel below a moisture content of 12%, and it may not even be parallel below the fiber saturation point. Parallelism below 12% moisture content implies that water is significantly compressed at moisture contents above 6% and uncompressed when between 0 and 6%. Curve D was drawn from the origin so as to meet curve C smoothly. It represents the minimum deviation from curve C that can reasonably represent the facts. It assumes that all of the void space within the cell wall is completely filled after the first 12% of water has been adsorbed.

Curve E is the differential curve obtained from integral curve D. Under these conditions, the initial compression would be only 0.04 cc. per g., which would give the initially adsorbed water an apparent density of 1.04 g. per cc. If all of the voids had a diameter not much larger than that of the water molecule, they could all be filled when 12% of water was taken up. If, however, the diameter of the voids in the dry cell walls varied from that of a water molecule up to several times that value, water would first be adsorbed only on the inner surface of the voids and would not completely fill them until capillary condensation in the largest void had been completed. This condition might not exist until the fiber saturation point (which is about 24% in the case of the cellulose sample under consideration) had been reached. Curve F represents such a case. The initial portion of curve F might have been drawn with a steeper slope. The form of the curve was selected so as to give a differential curve G, which represents a change in adsorption compression with moisture content that is practically equal to the change in differential heat of swelling with moisture content [13]. A rough proportionality between adsorption compression and heat of swelling has been shown to exist for other systems [14]. Curve G gives an initial compression value of 0.2 cc. per g. and an initial apparent density of the water of 1.25 g. per cc. Thus, when it is postulated that x-ray

* This equation, previously used by Stamm and Seborg [15], was erroneously reproduced in their publication by omitting the minus sign before the term $\frac{m_a}{D}$ and the parentheses.

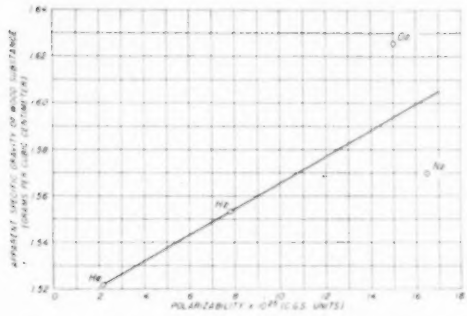

FIG. 4. *Relationship between the apparent specific gravity of Sitka spruce wood as measured in different gases and the polarizability of the gases.*

measurements, rather than a nonswelling liquid, reveal the true volume of cellulose substance, the apparent density of the initially adsorbed water is changed from the improbable value of 3.33 grams per cubic centimeter to the quite reasonable range of 1.04 to 1.25.

It is now generally believed that hydrogen bonding exists between water and cellulose. Hydrogen bonding involves electron displacement, and electron displacement could readily result in a decreased volume of the order just estimated. Orientation of water molecules alone might also account for the apparent compression. It thus seems unreasonable, considering the data at hand, to rule out the possibility of adsorption compression, as a number of investigators have done.

Other Support for the Theory of Packing of Adsorbed Molecules

From adhesion-tension measurements of liquids on solids, Bartell and Osterhof [2] and Bartell and Jennings [1] have shown that the work of adhesion of liquids to the solids that they wet is slightly greater than the work of cohesion of the liquid. The ratio of the work of adhesion of water to silica, aluminum oxide, barite, and calcium fluoride to the work of cohesion of water varied between 1.058 and 1.065. If it be assumed that cellulose will give a similar value and that the attractive forces are proportional to the work values (internal pressure of water increased from 12.50 to 13.27 kilobars, or an increase of 0.77 kilobar), the specific volume of adsorbed water up to the fiber saturation point would be 0.97, according to Bridgeman's [3] data for the compression of water. If the difference between the specific volume of cellulose as determined by x-rays and by water displacement represents the compression of adsorbed water at the fiber saturation point (24%), then the specific volume of the adsorbed water would be 0.97, as was predicted

$$\left(1.000 - \frac{(0.629 - 0.622)}{0.24}\right).$$

Another indication that adsorption compression occurs may be obtained from the data of Stamm [12], which show that the apparent specific gravity of Sitka spruce wood increases in order in helium, hydrogen, nitrogen, and oxygen. If the differences in the apparent specific-gravity values were due only to differences in the permeability of the voids, the order of increasing specific gravity would be nitrogen, oxygen, helium, and hydrogen, for the small molecules would be expected to fill the voids more readily. If the differences in apparent specific gravity are due to differences in compressive adsorption, and if the attractive forces are assumed to be proportional to the polarizability of the gases, the relationship shown in Figure 4 is obtained.* This correlation is much better than that obtained on the basis of molecular size. The fact that nonswelling oxygen gives an apparent specific gravity of cellulose which is greater than that measured in water can be explained only if oxygen is much more highly compressed when it is absorbed than is liquid water.

Summary and Conclusions

The specific volume calculated from x-ray crystal-structure data comes the nearest of the various available values to representing the true specific volume of cellulose substance.

Nonswelling liquids with relatively small molecules, such as benzene, measure the volume of the fibers or of the fiber walls, depending upon the accessibility of the fiber lumen. They do not enter voids within the cell walls.

Helium, and benzene that has replaced a swelling medium, penetrate voids in the noncrystalline zones of cellulose and approach the same specific-volume values as those calculated from x-ray data.

Water penetrates all void structures represented by the difference between specific volume measured in benzene and that calculated from x-ray data.

* Suggested by Dr. Harold Tarkow of the U. S. Forest Products Laboratory.

From the data presented, it appears that the volume represented by the difference between the specific volume calculated from x-ray data and that measured in water represents a contraction of water as a result of electron displacement and hydrogen bonding, rather than a more complete mechanical penetration of voids.

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INDUSTRIAL SECTION

Some Felting Properties of Wools of Different Geographical Origins*

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I. Introduction

It is generally believed that wools may differ considerably in the rate or extent to which they will felt in a fulling mill or stocks. This property is often a basis for the selection of wools for blends, particularly in the manufacture of felts, where the feltability is obviously an important economic consideration. Not only are such differences in feltability widely recognized but measurements supporting their existence have often appeared in the literature [2, 5, 8, 9].

The available evidence concerning differences in feltability of different wools refers to severe felting action of the type which occurs in a fulling mill or stocks. There is need for information of this type as it applies to ordinary laundering, and indeed it might be anticipated that knowledge of this sort might throw new light on the problem of producing shrink-resistance in wool garments. The present investigation, undertaken with this thought in mind, concerns the felting of different types of wool during laundering, or during the top shrinkage test, the results of which have been shown to correlate well with the results of laundering tests [1]. It should be clearly understood that the results presented below do not refer to felting of the type which occurs in a fulling mill or stocks.

In order to obtain wools which might be expected to felt differently, samples were obtained from different parts of the world, several types being included on the basis of their reputation for high or low feltability. These samples were then evaluated, principally in the form of "pure" tops, which contained only the single type of wool, rather than a blend. The evaluation included a number of measurements of mechanical and frictional properties of the fibers as well as tests of felting behavior, in order to determine whether the latter property might be explained in terms of the former ones. While large differences in felting behavior were not realized, the results appear to be of sufficient general interest to warrant their presentation.

II. Materials and Methods

Eleven wools representing a variety of sources were scoured with soap and soda ash, carded, and combed in accordance with typical good mill practice. The 11 "pure" tops were identified by source and fineness, as follows:

1—Texas 70's; 2—Australia 64's; 3—Australia 62's; 4—Texas 64's; 5—Montevideo 64's; 6—"Domestic" Pulled 62's; 7—Australia 58/60's; 8—New Zealand 62's; 9—Argentina (Corrientes) 60's; 10—Brazil 58's; 11—Buenos Aires 58's.

The feltability of the tops was determined by a top shrinkage test which involves measurement of the change in length of a sliver when it is tumbled for varying times in a revolving jar [1]. The severity of the test could be varied by changing the level of the liquor in the jar; tests were made using 1 liter and 5 liters of water, subsequently identified herein as the "severe" and the "mild" top shrinkage tests. Measurements were made after 4, 10, and 20 min. of

* This work constitutes a part of the Army Quartermaster program on shrink-resistance of wool for military clothing, which is under the supervision of the National Research Council Advisory Committee on Textile Finishing Research.

TABLE I. FELTING BEHAVIOR OF TOPS FROM DIFFERENT SOURCES IN A SEVERE TOP SHRINKAGE TEST

Sample No.	Source	Nominal grade	Top shrinkage in: 4 min. (%)	10 min. (%)	20 min. (%)
1	Texas	70's	19	37	50
2	Australia	64's	19	35	45
3	Australia	62's	22	38	49
4	Texas	64's	19	38	52
5	Montevideo	64's	19	36	49
6	"Domestic" Pulled	62's	16	29	40
7	Australia	58/60's	23	42	52
8	New Zealand	62's	20	57	47
9	Argentina (Corrientes)	60's	19	37	49
10	Brazil	58's	20	38	51
11	Buenos Aires	58's	21	41	52
		Mean of 10 wools*	20	38	49.5

* Excluding sample 6.

TABLE II. FELTING BEHAVIOR OF TOPS FROM DIFFERENT SOURCES IN A MILD TOP SHRINKAGE TEST

Sample No.	Source	Nominal grade	Top shrinkage in: 5 min. (%)	15 min. (%)	30 min. (%)	90 min. (%)
1	Texas	70's	11	23	32	43
2	Australia	64's	16	32	40	49
3	Australia	62's	13	28	36	46
4	Texas	64's	9	20	29	39
5	Montevideo	64's	9	22	31	42
6	"Domestic" Pulled	62's	7	15	20	29
7	Australia	58/60's	12	27	36	46
8	New Zealand	62's	13	29	38	46
9	Argentina (Corrientes)	60's	11	24	32	42
10	Brazil	58's	10	21	29	39
11	Buenos Aires	58's	10	22	30	40
		Mean of 10 wools*	11.5	25	33.5	43

* Excluding sample 6.

tumbling, respectively, in the 1-liter test, and after 5, 15, 30, and 90 min., respectively, in the 5-liter test. The felting of socks made from 4 of the samples of top was also determined by a conventional test for laundering shrinkage, as described below.

Single-fiber stress-strain measurements were made on the various wools using an electronically controlled fiber extensometer [7]. The fiber diameters of the test fibers used were estimated by a gravimetric method. Fibers were extended 20% at a rate of 10% per min. and retracted at the same rate. The elastic parameters calculated included load at 20% elongation, work required for 20% extension, and work recovered on return from 20% extension. Frictional properties were measured with the fiber friction meter described by Frishman *et al.* [4].

III. Results and Discussion

The results are summarized in Tables I–IV inclusive.

In Tables I and II the shrinkage values for the various wools are grouped closely about the mean, indicating that, except for sample 6, all of the wools exhibit substantially similar felting behavior in the top shrinkage test. Sample 6, a domestic pulled

TABLE III. SINGLE-FIBER ELASTIC PROPERTIES OF WOOLS OF DIFFERENT ORIGINS

Sample No.	Source	Nominal grade	No. of fibers measured	Mean diameter (μ)	Load to extend 20% (g./den.)	Work for 20% extension (ergs/cm.^{3} $\times 10^8$)	Work recovered from 20% extension (ergs/cm.^{3} $\times 10^8$)
1	Texas	70's	16	21	0.31	0.55	0.27
2	Australia	64's	15	26	.34	.60	.32
3	Australia	62's	14	24	.56	.65	.34
4	Texas	64's	15	27	.37	.65	.35
5	Montevideo	64's	15	30	.37	.62	.33
6	"Domestic" Pulled	62's	16	26	.35	.61	.32
7	Australia	58/60's	17	30	.33	.57	.30
8	New Zealand	62's	16	28	.38	.68	.35
9	Argentina (Corrientes)	60's	14	24	.34	.61	.29
10	Brazil	58's	15	26	.34	.59	.30
11	Buenos Aires	58's	16	28	.35	.62	.33

TABLE IV. SINGLE-FIBER FRICTIONAL PROPERTIES OF WOOLS OF DIFFERENT ORIGINS

Sample No.	Source	Nominal grade	No. of fibers measured	Mean diameter (μ)	Coefficient of friction With-scale	Coefficient of friction Anti-scale	Friction difference
1	Texas	70's	18	21	0.24	0.45	0.21
2	Australia	64's	16	24	.27	.49	.22
3	Australia	62's	15	25	.28	.47	.19
4	Texas	64's	16	27	.24	.44	.20
5	Montevideo	64's	16	25	.23	.42	.19
6	"Domestic" Pulled	62's	15	26	.25	.44	.19
7	Australia	58/60's	21	28	.27	.46	.19
8	New Zealand	62's	15	28	.24	.43	.19
9	Argentina (Corrientes)	60's	17	25	.27	.45	.18
10	Brazil	58's	15	25	.28	.46	.18
11	Buenos Aires	58's	15	27	.27	.48	.21

wool, shrinks appreciably more slowly than the others.

The results of elasticity and of friction measurements, summarized in Tables III and IV, also indicate remarkable similarity in behavior among the 11 wools. Furthermore, sample 6, which seemed to be of relatively low feltability in this test, was not very different from the other 10 types with respect to elastic and frictional properties.

In view of the similarities in behavior among most of these wools, top shrinkage tests were run using samples of a variety of commercial tops which were available in the laboratory; these are usually blends of many types of wool. The results are summarized in Table V, and the shrinkage data for the commercial blends and the "pure" tops are plotted in Figures 1 and 2.

It is noteworthy that the shrinkage behavior is substantially identical for the commercial blended tops and the "pure" tops. A conspicuous exception is sample BF64, a French combed top of appreciably shorter staple than most of the other blended wools. This result led to a consideration of the effect of staple length on the shrinkage behavior.

Shrinkage as Related to Staple Length

It was shown by Speakman, Stott, and Chang [9] that, for milling with soap in the fulling stocks, fabrics made from long-staple Wensleydale wool shrank more than corresponding fabrics made from the same

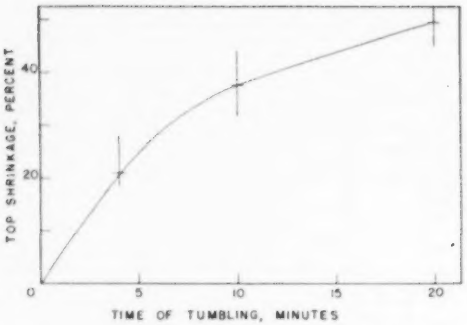

FIG. 1. *Rate of felting in severe top shrinkage test. Results for all "pure" tops except sample 6, and all commercial blends except sample BF64 are included. Vertical lines indicate range.*

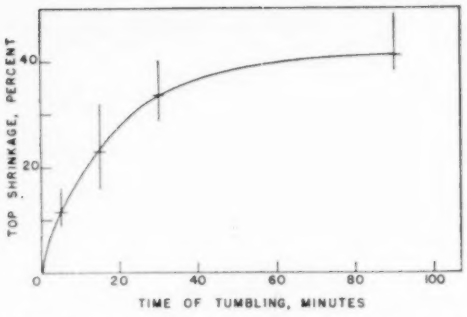

FIG. 2. *Rate of felting in mild top shrinkage test. Results for all "pure" tops except sample 6, and all commercial blends except sample BF64 are included. Vertical lines indicate range.*

wool which had been cut to a shorter staple length. In some later experiments with Australian Merino wools Speakman and Sun [10] obtained results which indicated the reverse to be true, although examination of their data in general shows small differences between the long- and short-fibered samples.

The fiber-length distribution of 10 of the special tops used in the present work was determined through the cooperation of the Barre Wool Combing Co., Ltd., by A.S.T.M. Method D 519–40, using the Suter apparatus. The data are given in Table VI, together with some corresponding top shrinkage values. While there is not a one-to-one correlation, long staple does appear to be associated with rapid felting in the mild top shrinkage test. Thus, samples 3 and 8, the longest-fibered wools, show high felting rates. Sample 6, which felts the least, has a short staple length. Sample 4 is moderately low in mean fiber length but contains a fair percentage of the longer fibers, which may account for the fact that its felting behavior approaches the mean for the group. It seems likely that, irrespective of the mean values, a minority of long fibers may be adequate to increase the feltability in the top shrinkage test, although this hypothesis requires better experimental confirmation than is available here. The top shrinkage-fiber length data are plotted in Figure 3, which illustrates the good over-all correlation between these two properties. Thus, in spite of the apparently anomalous behavior of samples 1 and 2, fiber length does appear to contribute in an important way to felting behavior in the top shrinkage test. In this connection it is interesting to reconsider sample BF64, the commercial top which exhibited a low degree of felting in the top shrinkage test. The mean fiber length of this sample was found to be 1.93 in., with only 0.7% of the fibers being 4 in. long or longer. This result may well account for the low feltability of this sample in the top shrinkage test. Additional experimental work in this direction would be desirable to elucidate further the effect of fiber length on laundering shrinkage.

Felting as a Function of Fiber Diameter

Until recently, there has been little clear-cut evidence concerning the relationship between fiber diameter and the felting of wool. Speakman and Stott [8] studied the milling of blends of 80's and 56's wools, their results suggesting that as the content of the coarser wool increases, felting decreases.

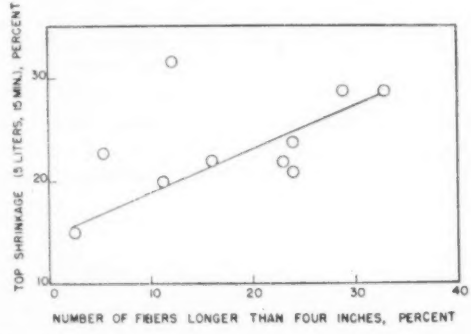

FIG. 3. *Top shrinkage as related to percentage of fibers longer than 4 inches.*

TABLE V. FELTING BEHAVIOR OF COMMERCIAL WOOL TOPS IN TOP SHRINKAGE TESTS

Sample No.	Nominal grade	Top shrinkage: Severe test 4 min. (%)	Severe test 10 min. (%)	Mild test 15 min. (%)	Mild test 90 min. (%)
A60	60's	23	38	21	37
L50	*50's	19	39	19	37
M56	56/58's	22	37	27	47
A56	56's	19	34	16	39
L70	64/70's	23	40	20	37
F70	70's	19	35	19	40
BF64	64's (French combed)	10	24	11	32
B64	64's	28	44	23	38
BA36	36's	21	32	23	42
C70	70's	21	36	19	38
	Mean of 9 wools*	22	37	21	38.5

* Excluding sample BF64.

Martin [6] has stated that there is little difference in felting behavior between 80's and 56's or lower. Dutton [3] has recently reported on laundering tests for a series of knitted fabrics in several constructions, made from wools ranging from 56's to 70's in quality. His results show that in the slackest construction the 56's wool felted less than the finer qualities, but in tighter constructions the differences between qualities were less apparent. A recent W.I.R.A. bulletin [12] disclosed the results of shrinkage in laundering of a series of hosiery fabrics made from "pure" tops of 56's, 64's, 70's, and 80's grades. The data indicate that the anticipated increase in felting with increase in grade is not realized; in fact, with continued laundering the shrinkage of the finest wool is least in this group of wools.

Since the 11 special wools studied in the present work did not encompass a very wide range of fineness, 2 commercial wools varying widely in grade were obtained. One was a 36's grade Buenos Aires top and the other was a 70's grade Cape wool (obtained through the courtesy of the Forstmann Woolen Co.), the latter being reported to be a wool which felts well in commercial fulling operations. The top shrinkage results for these samples are included in Table V (last two wools listed). The initial rates of felting are very similar to the means for the previous wools studied. It therefore appears from these results that grade of wool is not of itself an important factor in the shrinkage of wool top, or in the laundering shrinkage of wool.

TABLE VI. FIBER-LENGTH DISTRIBUTION OF "PURE" TOPS OF DIFFERENT ORIGINS

Sample No.	Mean staple length (in.)	Coefficient of variation (%)	Percentage of fibers longer than: 3 in. (%)	4 in. (%)	Top shrinkage (mild test) in 15 min. (%)
1	2.26	45	25	5	23
2	2.69	40	39	12	32
3	3.29	41	58	33	28
4	2.67	40	40	11	20
5	2.87	39	44	16	22
6	2.37	35	21	2	15
8	3.25	39	57	29	29
9	3.09	41	52	24	24
10	3.10	39	54	24	21
11	3.01	42	50	23	22

Laundering Behavior of Garments Made from Wools of Different Origins

The results of the top shrinkage test have been related elsewhere to the laundering shrinkage of garments made from untreated and shrink-resistant top [1]. However, in view of the small differences found among the various untreated wools tested here by the top test, it was considered desirable to confirm the relationship between laundering shrinkage of garments and the top shrinkage behavior of the "pure" tops. Accordingly, a 1/20 yarn was spun from 4 of the "pure" tops—samples 4, 5, 6, and 7—and the yarns were knitted into a 7×3 rib construction on the same machine. Laundering tests were performed on the socks in the gray, after relaxation, using a commercial type of reversing wash wheel,

TABLE VII. SHRINKAGE IN LAUNDERING OF SOCKS MADE FROM WOOLS OF DIFFERENT ORIGINS

Sample No.	Shrinkage in length of foot*: 1 hr. (%)	2 hr. (%)	Increase in shrinkage in additional hour of severe laundering† (%)
4	12	16	12
5	13	17	14
6	11	14	10
7	11	14	14

* Measured with the Schiefer device.
† Using hot water at 140° F.

soap as detergent, a low water level, and water temperature of 100°F.

The results of the laundering shrinkage measurements are shown in Table VII. These data confirm the indications of the top test, in that socks made from the "pure" tops felted to very nearly the same degree. It is interesting to note that the differences in felting shrinkage among the 4 wools are small compared with the effect which would be produced by a very mild shrink-resistant treatment.

IV. Summary and Conclusions

The felting behavior in a top shrinkage test of 11 "pure" tops has been investigated. Only small differences were found among the samples in the results of this test. A group of commercial blended tops which were studied by the same method exhibited correspondingly small differences in top shrinkage. Such small differences as were found are correlated with staple length, the longer fibers promoting felting in this test. Felting in the top shrinkage test was apparently unaffected by fiber diameter, a result which is in agreement with the findings of other investigators, who report that the laundering shrinkage of garments is not greatly affected by wool grade.

Laundering tests performed on socks made from 4 of the "pure" wools of different geographical origin revealed no appreciable differences among them. These results are consistent with the results of the top shrinkage test.

Differences between single-fiber mechanical and frictional properties of the 11 wools were also found to be quite small.

Acknowledgment

Grateful acknowledgment is made to Messrs. Levon Yacubian and John M. Gould of the Barre Wool Combing Co., Ltd., who very kindly provided the special tops used in this work, as well as the analyses of staple length. The assistance of Miss Martha L. Markovich and Mrs. Virginia Giles Moran in making many of the measurements is also acknowledged with gratitude.

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Effect of Weather on Bleached and Unbleached Cotton Duck

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AN EARLIER PUBLICATION [5] from this Laboratory discussed the changes observed in breaking strength and cuprammonium fluidity of several different cotton fabrics during extended exposure to weather in the warm, moist climate of New Orleans. Under such conditions closely woven gray (loom state) cotton goods proved to be much more susceptible to mildew than were fabrics of similar construction from which the noncellulosic constituents had been removed by scouring or scouring and bleaching prior to exposure. At points of equal strength loss fluidity values were usually lower in gray than in scoured or bleached cloth.

It was of special interest to observe the destructive action of weather on cotton duck, a fabric widely used in outdoor service. Gray army duck was included in the earlier tests; but at that time scoured or bleached duck of the same construction was not available. Since the behavior in weather exposure of the latter material is also a matter of commercial importance, comparative exposure tests of bleached and unbleached duck were later carried out, with the results herein reported.

Fabric and Test Methods

A standard 8-oz. army duck was selected for the test fabric. This cloth is woven with plied, unsized yarns, with a thread count of 52 warp by 40 filling, and usually weighs a little more than 10 oz. to the sq. yd. From a long piece of duck woven on the same warp yarns a portion was taken for scouring and bleaching and the balance was retained in the gray. Twenty-five yds. of the cloth were boiled off in open width on a jig for 3 hrs. in a 2.0% solution of caustic soda, rinsed well in hot water, and bleached at 150°F in a 0.5% solution of hydrogen peroxide adjusted to pH 11.0 by addition of sodium silicate. After bleaching, the cloth was again well washed, squeezed, and dried on a tenter frame.

Scouring and bleaching were closely controlled to keep chemical degradation to a minimum. A subsequent determination showed that the original fluidity of the gray cloth, 2.3 rhes, was increased to only 2.6 rhes after bleaching. The alcohol-soluble material present in the gray cloth was reduced in these operations from 1.25% to 0.52%, and the ash content from 0.95% to 0.06%.

Six 1-yd. samples cut from both the gray and the bleached duck were numbered consecutively, wrapped in paper, and stored in a dark locker until needed. Weather exposure tests were carried out in the manner described in the earlier paper [5]. The first samples of gray and bleached cloth were exposed on December 1, and at 2-mo. intervals thereafter replicate pairs were exposed, until the final, or sixth, set was placed on the exposure racks on October 1. Portions of all samples were removed for analysis at the end of each month, for a period of 12 mos.

Determinations were made of the changes that had occurred in the weathered samples in warp breaking strength, cuprammonium fluidity, pH of the water extract, and copper number.

Breaking-strength tests were made according to standard methods, using a pendulum-type machine and 10 raveled strip specimens for each test to give a reliable average. Before breaking, the specimens were conditioned in an atmosphere of 65 ± 2% relative humidity and 70 ± 2°F. All breaks were made on warp threads, and the strength losses were calculated as percents of the warp breaking strength in pounds of the original unexposed fabrics.

Fluidities were measured in reciprocal poises, or rhes. The cuprammonium reagent used contained 30 g. of copper per liter and met the specifications of the American Chemical Society [1]. The method

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employed was that described by Conrad and Tripp [4], which provides a velocity-gradient adjustment.

pH values were determined with a Beckman Model G pH meter equipped with glass and calomel electrodes; in each test 2.0 g. of finely ground cotton extracted with 20 ml. of freshly distilled water were used.

The method used for determining the copper number was that described by Heyes [9], except that the 0.04*N* solution of potassium permanganate was replaced by a 0.01*N* solution of ceric sulfate [2]. (Copper number is defined as the weight of copper reduced from the cupric to the cuprous state in alkaline solutions by 100 g. of dry cellulose.)

Test Results

General

The changes observed at 2-mo. intervals in strength, fluidity, pH, and copper number of the gray and bleached fabrics during 12 mos. of exposure to weather are shown in Figures 1, 2, 3, and 4.

It is evident that the two kinds of cotton materials responded differently in certain respects to the degrading action of weather, and that much wider variations in strength losses after equal periods of exposure occurred in the gray than in the bleached samples.

From the averaged results of the tests it was found that the gray cloth lost 75% of its original breaking strength and that its fluidity increased to 15.5 rhes, as compared with a strength loss of 55% and a final fluidity of 21 rhes for the bleached cloth. The copper number of the gray fabric increased from 0.37 to 1.76, as compared with values of 0.15 and 2.19 for the bleached, while the pH values, which were initially 7.18 (gray) and 8.05 (bleached), fell gradually to the nearly equal final values of 6.11 and 6.01.

Strength and Fluidity Changes

A study of the changes in breaking strength and fluidity which occurred in the successively exposed

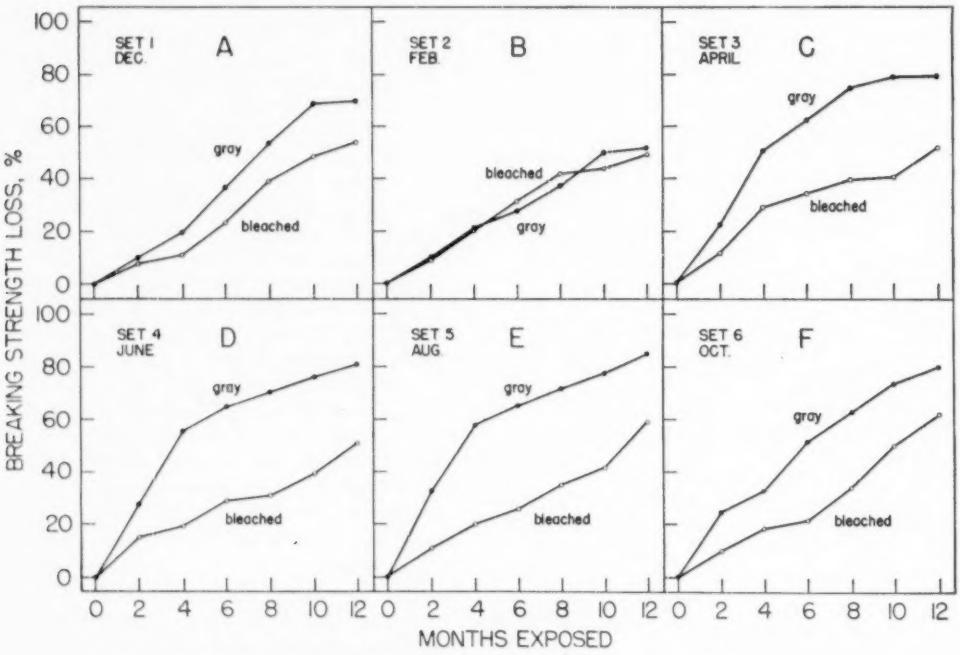

FIG. 1. *Effect of weather exposure on breaking strength of gray and bleached duck.*

pairs of samples helps to make clear the important part played in weathering by biological tendering of the unpurified cloth, as well as the marked degree to which this degradative factor may be influenced by the climatic conditions which prevail during the early stages of the tests.

It has been observed by several investigators [5, 8, 11, 12] that even severe tendering of cotton materials by the action of microorganisms is not accompanied by the corresponding increase in fluidity which is invariably caused by chemical degradation. Fargher [7] has pointed out that the tendering of relatively light, open cotton fabrics in weather exposure is due essentially to chemical (nonbiological) modification of the cotton, whether the fabrics have been scoured or not. The reason for this is that the leaching action of weather rapidly removes the noncellulosic materials from light fabrics of open construction and in a short time converts them to the equivalent of the scoured state, in which the cloth is much less susceptible to mildew. This is usually not true of duck, a closely woven fabric which retains more tenaciously the impurities of the gray cotton and as a result affords for a longer period abundant nutrition for microorganisms. However, it was found in the present tests that when conditions during the first few weeks of exposure were unfavorable to mildew, strength losses which occurred in both the bleached and the unbleached duck samples were of much the same order throughout the 12 mos. of exposure.

In Figure 1 the percent breaking-strength losses for the individual gray and bleached samples are plotted for each 2-mo. interval against time of exposure. The figure illustrates strikingly the influence of climatic conditions on biological activity during the weathering process.

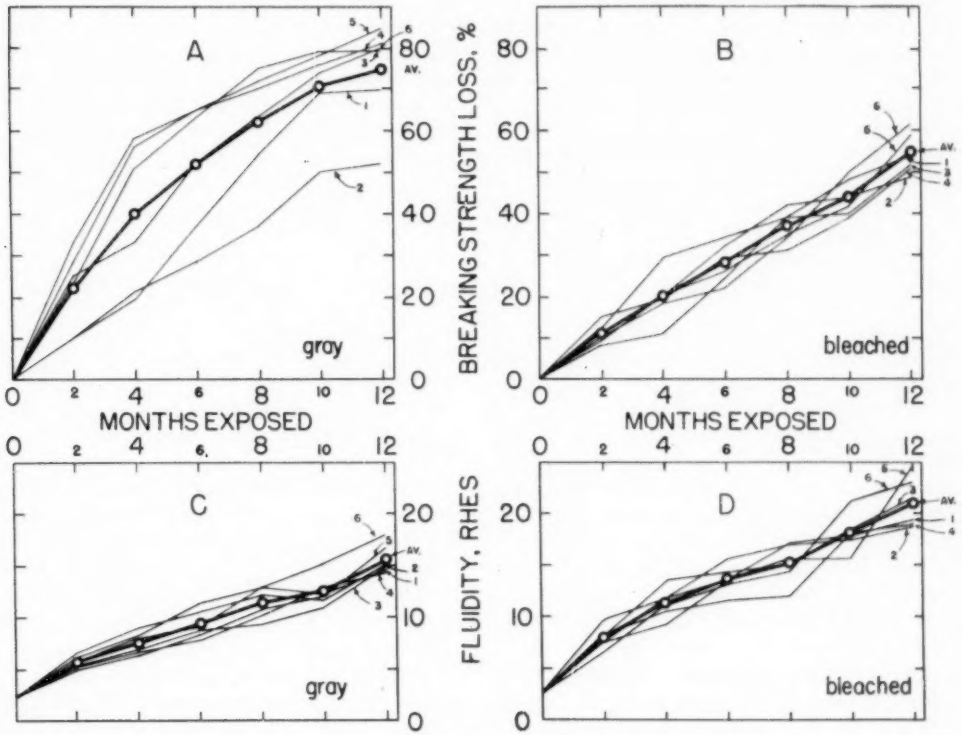

FIG. 2. *Breaking strength and fluidity changes in 6 gray and 6 bleached duck samples during weather exposure.*

The samples of Set 1 were put out to weather on December 1. This month proved to be unusually warm and humid, and mildew was visible in the gray sample after 2 or 3 wks. It is evident from the curves (Figure 1A) that the strength of the two samples diverged early in the test, and that the pattern of higher losses in the gray sample continued throughout the 12 mos. The difference was apparently due to what Fargher [7] has characterized as the greater mildew capacity of the unbleached cloth.

Set No. 2, put out on February 1, encountered cooler conditions. The average temperature for February was 9°F lower than that for the preceding December and there was much less moisture in the atmosphere, although both months had 61% of possible sunshine. It is of interest that the strength-loss pattern (Figure 1B) established for both samples under the cooler and drier conditions which prevailed in February carried through the entire 12 mos. of exposure without much divergence. Since at the beginning of this test atmospheric conditions were not favorable for biological activity, it may be assumed that by the time these conditions became more favorable the leaching action of rain had, in effect, converted the gray cloth to the bleached state. At the end of February the gray sample was almost free from mildew spotting, in contrast to the condition of the replicate sample exposed during December. Rather severe mildew spotting was detected in the gray sample after about 6 mos. of exposure, although, as previously noted, its strength losses during the test did not significantly exceed those of the bleached sample.

When Set No. 3 was exposed April 1, biological attack was immediate and by the end of the month the gray sample was heavily marked with mildew. The wide divergence in the strength-loss curves for the two samples as the test proceeded (Figure 1C) indicates the severity of the biological tendering which was suffered by the gray cloth. The same strength-loss pattern was repeated in the sets (Figures 1D, E, and F) which were put out in succession to weather during the warm months, but in the October set (No. 6) the divergence in strength losses between the gray and the bleached samples was somewhat less marked.

Figure 2 shows graphically the changes in breaking strength and cuprammonium fluidity which were observed in the different samples. There is sharp contrast between Section A, in which individual and average percent strength losses for the 6 gray samples are plotted against time of exposure in months, and Section B, in which the corresponding values are plotted for the 6 bleached samples. There were wide variations in the strength losses of the gray samples, due chiefly to seasonally influenced biological tendering, as compared with much more uniform strength losses in the bleached cloth, which had suffered almost no biological tendering.

Sections C and D of Figure 2 show similar plots for the fluidity increases which were observed in the gray and bleached samples during the tests. Since fluidity is not influenced by biological attack, the close grouping of the individual curves in these plots indicates that the effects of nonbiological tendering were much the same in both types of cloth.

It was evident that the average strength loss was lower and the fluidity increase was higher in the bleached than in the gray samples. Since in the same sets the gray and the bleached samples received equal amounts of sunlight, the consistently higher fluidity values for the bleached cloth suggest that the slight chemical damage received in the pretreatment may have rendered this cotton somewhat more sensitive to the photochemical action of sunlight. A record of the radiant solar energy received by all sets of samples during their 12 mos. of exposure showed no very large differences in the totals:

Set No.	Exposure begun	Total energy received (g.-cal./cm.^{2})
1	December	148,760
2	February	136,830
3	April	142,030
4	June	151,830
5	August	144,660
6	October	149,630

pH

The higher pH observed in the bleached duck before exposure was probably due to the rather alkaline water used in scouring and bleaching. This difference was rapidly lessened by the action of weather, and after a few weeks of exposure the reactions of the bleached and the gray fabrics were about the same. During the remainder of the test pH values for both sets of samples decreased gradually to the final average readings of approximately 6.0 (Figure 3).

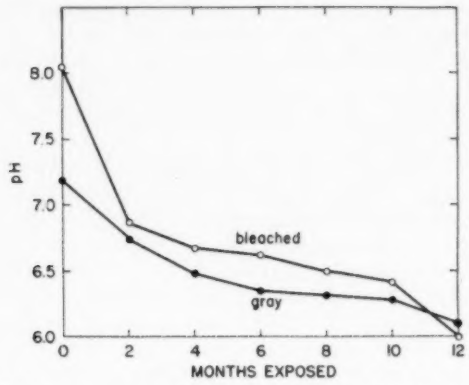

FIG. 3. *Averaged pH changes in 6 gray and 6 bleached duck samples during weather exposure.*

Copper Number

In Figure 4 the averaged copper numbers of the 6 gray and 6 bleached duck samples are plotted against time of exposure. It is evident that the initially lower number of the bleached cloth increased more rapidly than the number of the gray during the first 6 wks. of weathering, at the end of which the values were approximately equal. Through the remaining months of the test the value for the bleached cloth was consistently higher. The variations in copper numbers determined for the individual samples (not shown in Figure 4) were of much the same order as the corresponding fluidity variations plotted in Figure 2.

The copper number of the gray cloth before exposure was 0.37, compared with a corresponding number of 0.15 for the bleached cloth. The difference of 0.22 between these values probably approximates the "soluble" copper number defined by Fargher [7] as the difference between the copper numbers of raw cotton before and after washing. This value, he believes, may be used to assess fairly accurately the capacity of unpurified cotton to support the growth of microorganisms. The water-soluble constituents of the gray cloth evidently possess considerable reducing power, and their presence accounts for the higher initial copper number of that fabric.

Dorée [6] states that when the cellulose is normal the copper number is of the order of 0.2 or lower, but that any change in the cellulose through the action of heat, acids, alkalies, or oxidizing agents is revealed by a marked increase in this value. The fact that the copper number of 0.15 determined for the bleached duck is well within Dorée's range of values for unmodified cotton, together with the fact that a small fluidity increase was observed in the same material, confirms the conclusion that this fabric suffered only slight chemical degradation during scouring and bleaching.

Caution should be used in attempting to correlate the changes in copper number of exposed cotton with the degradative effects of weather, because of the complexity of the chemical changes that may occur in the cellulose. In general, it may be safely assumed that increase in copper number during exposure indicates the progressive formation of aldehydic reducing groups. However, Conrad and Kettering [3] have pointed out that during oxidative degradation of cotton the copper number often increases to a maximum and then decreases as further oxidative action occurs. It thus appears that aldehydic groups formed in the first stage of the action may be further oxidized to acidic (carboxylic) groups

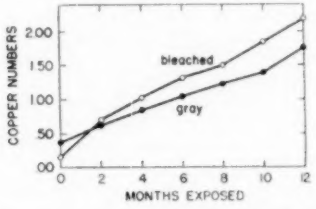

FIG. 4. *Averaged changes in copper number of 6 gray and 6 bleached duck samples during weather exposure.*

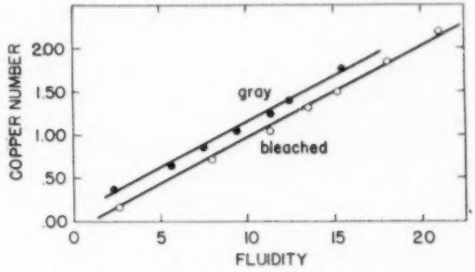

FIG. 5. *Copper number-fluidity relationships of gray and bleached duck samples during weather exposure.*

more rapidly than additional aldehydic groups are formed, in which case the initially increased copper number would tend to fall.

In the present tests the copper numbers of both gray and bleached duck increased continuously during the 12 mos. of exposure. This pattern conforms, generally, with that of the cuprammonium fluidities for the same fabrics (Figure 2), and it may be assumed that here the copper numbers serve as measures of a chemical modification of the exposed cotton which involved progressive formation of aldehydic groups, unaccompanied by formation of sufficient acidic groups to decrease significantly the reducing power of the degraded cellulose. The nearly linear relationships which exist between the averaged copper numbers and cuprammonium fluidities of the exposed samples are shown in Figure 5.

Of interest in this connection are the changes which occurred in the copper number of highly purified cotton yarn during atmospheric exposure in Southwestern England, as reported by Race [10]. From an original value of approximately 1.3 there was a gradual and practically linear increase during 20 wks. of exposure to a maximum of 4.9, which corresponded to a loss in breaking strength of 50%. Although initially and at points of equal strength loss the copper numbers which Race observed for the exposed yarns were considerably higher than those reported here for the bleached duck samples, there was a close resemblance between the fluidity-copper number relationships of the two types of materials within the comparable range of fluidity values.

Summary

Six replicate samples each of gray and of bleached cotton duck were exposed to weather for a total period of 12 mos.; the sets, each consisting of 1 gray and 1 bleached sample, were put out at 2-mo. intervals, the first on Dec. 1, the last on Oct. 1. Changes were observed in breaking strength, cuprammonium fluidity, pH, and copper number during exposure.

In the gray cloth the average strength losses were higher and the individual losses were more erratic than those in the bleached samples under similar conditions of exposure, a result attributed to the nonuniform and seasonally influenced attack of microorganisms to which the unbleached fabric was especially sensitive. In contrast, the average fluidity increase was less for the gray than for the bleached cloth, while variations in the fluidity changes of individual gray samples were not more marked. The pH values decreased gradually and at a fairly uniform rate from a high of approximately 8.0 for the bleached cloth to a low of approximately 6.0 for both fabrics.

The initially higher copper number of the gray duck was attributed to the presence of noncellulosic materials, which were readily removed by water. After a relatively brief period of exposure the averaged copper numbers of both fabrics were equal, and after that period that of the bleached cloth was consistently higher. The fairly uniform increase in these values during exposure indicated a progressive formation of aldehydic reducing groups. A practically linear relationship was observed to exist between the rise in copper number and the corresponding rise in fluidity for both the bleached and the unbleached fabrics.

Acknowledgment

Acknowledgment is made to Samuel G. Gremillion, Jr., who assisted in the outdoor exposure tests and in the determination of copper numbers and pH values; to Leila D. Wiggins and Janice Poynot, who determined the breaking strengths; and to Jean M. Santenac and Gloria A. Gautreaux, who made the fluidity measurements.

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The Measurement of Fabric Wrinkling

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A NEW INSTRUMENT to measure the wrinkle-resistance and wrinkle-recovery of fabrics has recently been constructed and tested in these laboratories. This instrument offers an accelerated method of analyzing fabrics which have been deformed by the random type of wrinkling which occurs under service conditions. In some respects, it resembles the Brush Surface Analyzer, the Physicists Research Company's "Profilometer," and other instruments which measure surface contours. The purpose of this paper is to describe the instrument, which we have named the "Wrinklometer," and to indicate its performance and potentialities.

Discussion

Procedure for Wrinkling Sample

Fabrics are wrinkled by a standardized procedure. A 10 in. × 4 in. fabric sample is stuffed in a random fashion into a glass test tube of 28-mm. inside diameter. The sample is held under a pressure of 5 lb. per sq. in. for 3 hrs. by means of a 4.4-lb. cylindrical weight which slips into the test tube on top of the fabric sample. The fabric is then removed and tested as described below.

Analysis of the Wrinkled Sample

The apparatus for measuring the wrinkles is shown photographically in Figure 1. The 10-in. × 4-in. wrinkled fabric is placed on a movable platform which is driven horizontally at a rate of 6 in. per min. by means of a long screw which is attached through a rubber shock link to a variable-speed motor. To each corner of the fabric is attached a small thread which supports a 5-g. weight in order to keep the fabric suitably positioned on the platform. The threads are held at 45° to the principal axes of the platform and are guided over the corners with small pulleys. As the platform is driven forward a small counterbalanced probe moves over the fabric and actuates a shutter between the light source and a General Electric photovoltaic cell. This cell is connected to a Leeds and Northrup "Speedomax" recorder. The contour of the wrinkled fabric is reproduced on the recorder paper. There is a one-to-one correlation between every wrinkle in the fabric and every peak in the curve as well as between corresponding wrinkle and curve heights. The area under the traced curve is proportional to the product of the mean wrinkle height and the length of the trace on the fabric. This area can be converted to the mean wrinkle height, $\bar{h}$, of the fabric. The instrument also has an electronic integrator which simplifies the calculations of mean wrinkle height. A description of the integrator is to be published elsewhere.

Four different traces are obtained on each sample by moving the platform laterally with an adjusting screw. These traces, each of which is 8 in. long, can be made without moving either fabric sample or tracer arm. With the aid of statistical analysis, four traces were selected as the minimum number for significant results. An 8-in. bar, fastened to the bottom of the moving platform, operates a microswitch which starts and stops the recorder. A clutch mechanism is used to set the platform in motion, but no record is made until the bar hits the microswitch. The clutch automatically disengages when the platform reaches the end of the screw drive. The instrument rests on rubber shock mounts which minimize the effect of internal vibrations.

The procedure for a routine analysis of a wrinkled sample is as follows: The instrument is calibrated by making a trace of a flat metal plate $\frac{9}{32}$ in. thick. An unwrinkled piece of the fabric is then placed on the platform. Obviously, the wrinkled fabric will vary in length and width because of the variable wrinkle height; however, excessive wrinkling has never reduced the length below 8 in. The process is then repeated four times on a wrinkled sample, the platform being placed in a new lateral position

each time. "Speedomax" traces are kept as permanent records which can be checked by means of a planimeter. When calculations are made from the records, the following relation is used:

$$\bar{h} = \frac{(A_w - A_c)}{(A_p)} \times \tfrac{9}{32} \times 25.4,$$

where A_w = average area under trace of wrinkled fabric, A_c = area under trace of unwrinkled fabric, A_p = area under trace of calibration plate, $\frac{9}{32}$ = calibration factor, and 25.4 = conversion factor (from inches to millimeters).

Since the planimeter method is time-consuming, an electronic integrator has been attached to the instrument. The electronic integrator operates simultaneously with the "Speedomax" recorder through the same bar-and-microswitch arrangement. The integrator makes use of a capacitor arrangement and pulsing circuit.

After each Wrinklometer analysis, the fabric sample is suspended from a wire with clips for 24 hrs. to permit it to recover under its own weight, after which four more traces are made. This process is repeated for 5 successive days. The results are then plotted as mean wrinkle height (mm.) *vs.* time (days). In addition to the graph, two empirical relations have been designated as measurements of the wrinkle-resistance and wrinkle-recovery. They are as follows:

Wrinkle-resistance index: $10/\bar{h}_0$ (mm.$^{-1}$)
Wrinkle-recovery index: $100(\bar{h}_0 - \bar{h}_4)/\bar{h}_0$ (limits: 0–100)

where h_0 and h_4 are the mean wrinkle heights immediately after wrinkling and after 4 days' recovery, respectively. Large values of both indices are desirable for resilient fabrics. Values of the wrinkle-resistance index usually range between 1 and 40.

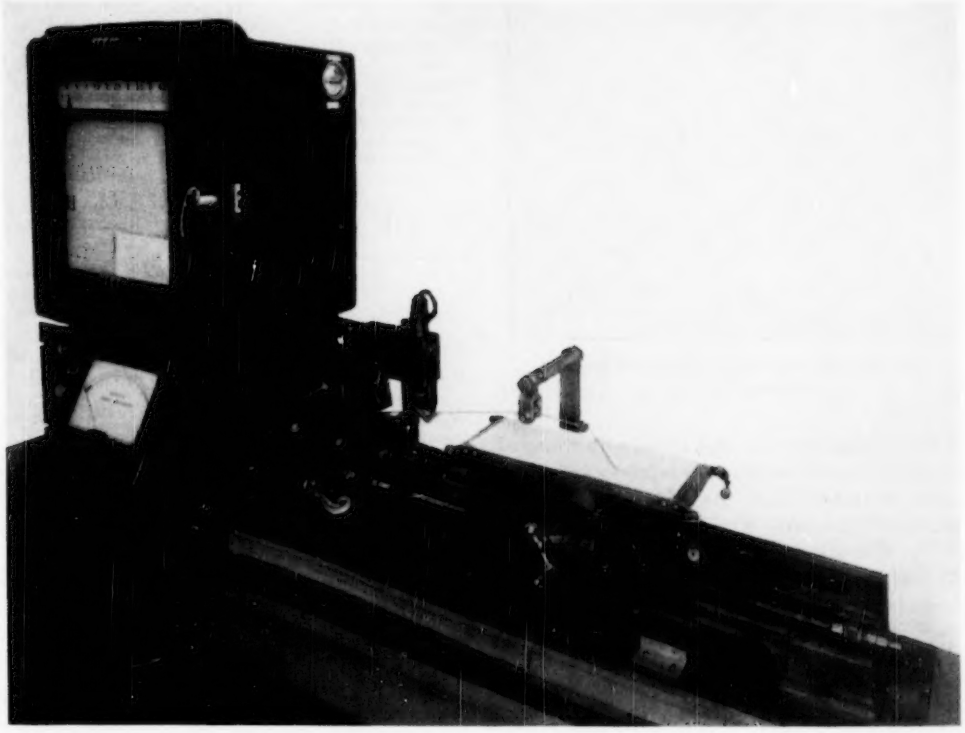
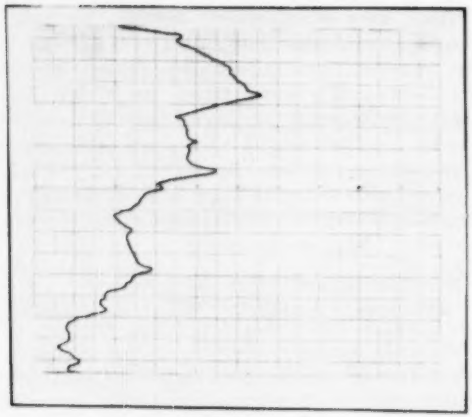


FIG. 1. *Photograph of the Wrinklometer.*



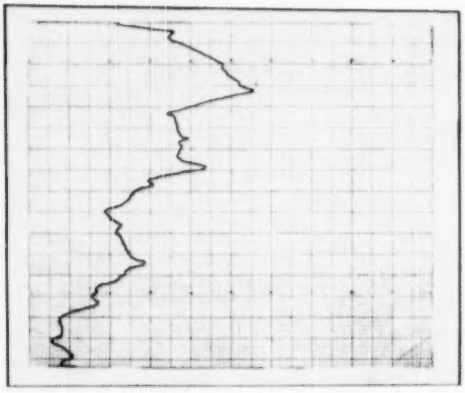


FIG. 2. *Graphs showing reproducibility of Wrinklometer traces.*

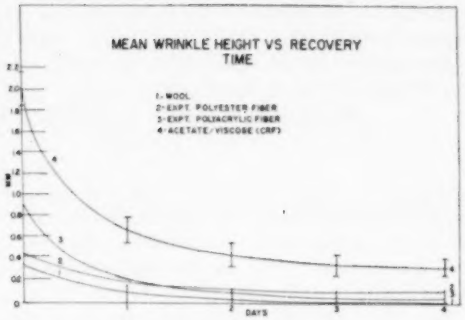


FIG. 3. *Curves for mean wrinkle height vs. recovery time for 4 fabrics.*

TABLE I. WRINKLOMETER RESULTS FOR FABRICS OF DIFFERENT CHEMICAL TYPES

Fabric composition	Mean wrinkle height (mm.) after: 0 day	1 day	2 days	3 days	4 days
Wool	0.34	0.10	0.03	0.03	0.03
Experimental polyester fiber	0.48	0.20	0.14	0.12	0.12
Experimental polyacrylic fiber	0.92	0.19	0.10	0.06	0.05
Acetate/viscose (crease-resistant finish)	2.05	0.64	0.42	0.36	0.36

TABLE II. WRINKLE-RESISTANCE AND RECOVERY INDICES FOR THE FABRICS OF TABLE I

Fabric composition	Wrinkle-resistance index, $10/\bar{h}_0$ (mm.$^{-1}$)	Wrinkle-recovery index, $100\,\frac{(\bar{h}_0 - \bar{h}_4)}{(\bar{h}_0)}$
Wool	29	91
Experimental polyester fiber	21	75
Experimental polyacrylic fiber	11	95
Acetate/viscose (crease-resistant finish)	5	82

The Wrinklometer has been tested with a limited number of fabrics to indicate the reproducibility and ranges of applicability. Examples of trace and sample reproducibility are illustrated in Figures 2 and 3. The standard deviations of the samples, which are represented by the lengths of the bars in Figure 3, are somewhat high and attempts to remedy this are now in progress.

Results for the fabrics in Tables I and II illustrate how the Wrinklometer separates fabrics of different chemical types on the basis of wrinkle-resistance and recovery. Each of the fabrics contains spun yarns of 2/32 worsted count, with approximately 14 turns per in. in both singles and ply, and is of tropical worsted weave with a count approximately 48 × 39. The mean wrinkle heights, $\bar{h}_t$ (mm.), after t days are given in Table I and are plotted in Figure 3.

The wool fabric shows the best resistance of any in the group, while the acetate/viscose fabric, even with a crease-resistant finish, shows the poorest. The wrinkle-resistance and wrinkle-recovery indices derived from Table I are reported in Table II.

Since high values of either index represent favorable performance, wool shows itself to be an outstanding fabric, with both high resistance and high recovery. The fabric made from the experimental polyester fiber has excellent resistance, while that made from the experimental polyacrylic fiber has excellent recovery. Neither matches the wool sample in both resistance and recovery. However, it is known that yarn and fabric construction variables contribute significantly to the test results and that the results of Table II can be changed to some extent by altering the constructions.

Summary

A new type of fabric testing apparatus, called the Wrinklometer, is described and shown to be useful for characterizing the wrinkle-resistance and recovery of fabrics. Fabrics are wrinkled in a random manner to simulate service tests and are then analyzed with the photocell-and-recorder arrangement of the Wrinklometer in such a manner that two numbers can be given to indicate the wrinkle-resistance and wrinkle-recovery of the fabric. Experiments are briefly described which indicate the reproducibility of the results and applications of the instrument.

Acknowledgment

The authors wish to acknowledge the helpful suggestions and services of a number of du Pont personnel, in particular of L. F. Beste, L. P. Haner, R. M. Hoffman, J. T. Rivers, and F. H. Thompson.

(Manuscript received March 24, 1950.)

Influence of Fiber Ends on the Adhesion of Bare Tire Cords

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Chemical and Physical Research Laboratories, The Firestone Tire & Rubber Company, Akron, Ohio

Abstract

1. Comparison of results on 100% cotton and 100% rayon-staple cords, neither being coated with an adhesive dip, indicates that the former have about 25% better adhesion. Since the advantage cannot be due to the presence of fiber ends protruding from the cord in one case and not the other, it is concluded that the superior adhesion of the bare cotton cord is in part due to a surface chemical or geometric property of the cotton fiber.

2. Comparison of results on 100% rayon-staple and continuous-filament cords, obtained from the same supplier, show that the staple-fiber product has about 60% better adhesion than the continuous-filament cord. This result indicates that, as has been frequently claimed in the literature, the presence of fiber ends in a tire cord does contribute toward improving adhesion. A 100% improvement in adhesion would be required, however, to show that only the lack of fiber ends curtails the adhesion of bare, conventional rayon cords.

WHILE the universal use of adhesive dips on rayon cords by the manufacturers of pneumatic tires has provided adequate, if not superior, bonding between the cord fabric and the rubber body stock of tires, it is well known that without the use of these dips the adhesion of rayon is entirely inadequate, and far inferior to that of bare cotton cord. For years the theory has prevailed in many quarters that the advantage which cotton has over bare rayon cord in adhesion is due primarily to the "fuzziness" provided by the many cotton-fiber ends which, projecting from the cord, become embedded in the soft rubber skim stock during calendering, and are firmly locked in place during vulcanization [1, 2, 3].

It has been supposed that continuous-filament rayon has the lower adhesion because it has no fiber ends which can tie it to the surrounding rubber, and that what adhesion it does exhibit is due to a weak chemical bond, plus the effect of the cable twist. While these ideas have been advanced in patent and technical literature, no experimental evidence appears to have been published showing to what extent the additional adhesion of cotton depends on the presence of fiber ends.

Alles [1] showed that the adhesion of continuous-filament cord could be substantially improved by intertwining in the filaments staple fibers with projecting ends. Not yet eliminated by experimental proof is the possibility that the superior adhesion of raw cotton is in part due to surface properties peculiar to it, which would themselves enhance chemical adhesion. There is also the possibility that the contrasting surface geometries of cotton fibers and rayon filaments also may have a significant influence on their mechanical adhesion.

To initiate clarification of these points, an experiment involving the measurement and comparison of the static adhesions of bare cotton, staple-rayon, and continuous-filament rayon tire cords was undertaken. Although the results would have no immediate practical interest, it was expected that they would provide information pertaining to the basic nature of cord adhesion, which, in turn, should indicate avenues along which improvements might be sought.

Experimental Procedure

For purposes of this study two experimental samples of tire cord, using $1\frac{3}{8}$-in. staple rayon, provided by the American Viscose Corp., were employed. In one of the samples the rayon staple was blended with an equal quantity of cotton, while in the other 100% rayon staple was used. Conventional cotton constructions were used, but with rayon staple the

TABLE I. STATIC "H" ADHESION TO RUBBER OF BARE CORDS OF COTTON AND STAPLE AND CONTINUOUS-FILAMENT RAYON

Fiber type	Cord sample: Construction	Ply twist (t.p.i.)	Cable twist (t.p.i.)	Gage (mils)	Specific adhesive force (lbs./in.)	Characteristic adhesion (p.s.i.)
100% cotton	12/4/2	17.42	10.91	33.0	36.5	1,106
50% cotton-50% rayon staple; 1 $\frac{3}{16}$-in.	10/4/2	16.25	10.15	33.8	34.4	1,018
100% rayon staple; 1 $\frac{3}{16}$-in.	12/4/2	11.80	10.22	27.6	23.8	864
100% rayon; continuous-filament	2200/2	10.25*	8.3*	34.7	18.9	542

* Estimated.

12/4/2 construction has a much lower gage than with cotton. A cotton cord of this construction, as well as 2200/2 continuous-filament cord from the same rayon supplier, was included in this study to permit the desired comparisons.

Adhesion was measured according to the "H"-test procedure [3], except that the cords were cured in a solid rubber pad 6 in. × 6½ in. × $\frac{1}{10}$ in. instead of the conventional grid-like pad consisting of separated strips of rubber connected laterally by the embedded test cords. "H" specimens of the regular type and size were stamped from the pad, the sheath of rubber around the cord between the end-strips of the "H" specimens being removed. A natural-rubber body stock was used for the pads. The final "pull-out" tests, employing clamps of the prescribed design, were made on a Scott X-3 machine operating at 12 in./min. In this study only the room-temperature static adhesions were obtained.

The results of the adhesion tests on the four samples, along with pertinent features of the cords, are recorded in Table I. The *characteristic adhesion*, which is tabulated in the last column, introduces a correction for differences in gage which is ignored in the calculation of the specific adhesive force [reference 3, page 38]. By means of the characteristic adhesion the bonding properties of different cord surfaces may be compared on the basis of unit effective surface area.

Discussion

It is readily seen that there is a steady decline in the adhesion to rubber of the bare cellulose cord as one goes from cotton, through staple rayon, to continuous filament. Even though the difference in adhesion between the 100% cotton cord and the 50–50 blend and that between the two 100% rayon samples are not in themselves highly significant statistically, taken as part of the whole set of data they substantiate the trend shown.

The question arises whether, in addition to factors already noted, differences in cable twist can account for the low adhesion of the rayon samples. It has been shown that in 2-ply cotton cords of comparable gage changes in cable twist from 7.25 to 15.70 t.p.i. produced an extreme change in characteristic adhesion of only 12% [reference 3, page 36, Table 17]. Thus the difference in cable twist between the all-cotton and the 50–50 sample in Table I cannot be considered important.

Considering now the all-cotton and the all-rayon staple samples, between which the difference in adhesion is substantial: it is true that the lower gage of the latter diminishes the influence on adhesion of whatever twist the cord has. This follows from the fact that for a given twist the helical angle diminishes with decrease in gage, and helical angle is the factor directly affecting adhesion (though only slightly). Even here, however, after the correction for gage differences which the characteristic adhesion introduces, a correction for twist would bring the value for the 100% rayon staple up to not more than 880 p.s.i.

Comparing the results in Table I on the two 100% rayon cords, it is seen that the introduction of fiber ends only, without alteration of essential features of the filament surface, raised the characteristic adhesion to 864 p.s.i. from 542 p.s.i. for continuous fila-

ments, a 60% increase. Thus there is an indication that fiber ends protruding from a cord do contribute toward increasing the adhesion.* When, however, a change in fiber type (to cotton) was included in the change to staple, the characteristic adhesion rose to 1,106 p.s.i., representing a 100% improvement over the adhesion of the continuous-filament sample. Viewed another way, these same data show that the all-cotton sample has 25% better adhesion than the all-rayon staple. Examination of the three staple-fiber cords under a microscope failed to disclose any discernible difference in the "fuzziness" of the cord surfaces, although the sheen of the individual rayon fibers was observed.

* In order to minimize the influence which rayon finish might have on the adhesions in this comparison, the continuous-filament control was obtained from the same supplier who had furnished the staple-rayon sample. It is not known definitely, however, that the same finish was used on the two samples.

Acknowledgment

Thanks are due to the Firestone Research Management for the release of the information contained in this contribution.

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(Manuscript received July 5, 1950.)

Letters to the Editor

The Preparation of Water- and Alkali-Soluble Cotton Yarns

Abstract

Reports in the public press have confused the two types of soluble yarns produced in the Southern Regional Research Laboratory. This letter differentiates between the alkali-soluble metal carboxymethylcellulose fibers previously described and the new water- or alkali-soluble modified cotton yarns. A typical method of preparation is described.

SOUTHERN REGIONAL RESEARCH LABORATORY *
2100 Robert E. Lee Boulevard
New Orleans 19, Louisiana

May 26, 1950

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A previous publication in this journal [8] described the preparation and properties of alkali-soluble metal carboxymethylcellulose fibers prepared by extrusion. This material and process were patented [9] and also received considerable attention in the daily press. Since that time another development of the Southern Regional Research Laboratory, a carboxymethylated cotton yarn, prepared by direct etherification, which is water-soluble as well as alkali-soluble, has also been described in the newspapers. However, the distinction between these two research products has not been plain to all readers. This communication is intended to clarify the matter to textile chemists and manufacturers and also to give information on the soluble yarn in advance of a more detailed publication.

Briefly, the distinction between the two products lies in the method of production and in the starting materials. The alkali-soluble fiber is made by extruding a solution of sodium carboxymethylcellulose into a coagulating bath containing a metal salt the metal of which reacts with the long-chain modified cellulose to form a water-insoluble salt. The polymer thus formed by cross-linking with the metal makes the water-insoluble fiber. This process is similar to the process used in making rayon.

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The carboxymethylated cotton yarn, on the other hand, is made by treating ordinary cotton yarn so that it becomes soluble in water and in dilute alkali while changing but little in form and retaining most of its original fibrous characteristics.

Interest in soluble fibers and yarns has been stimulated in this country by descriptions [1, 3, 5] of the numerous uses to which soluble alginate fibers have been put in England—in novelty fabrics, lightweight woolen goods, imitation astrakan materials, the connecting yarn in the String Sox process, and other applications. A method of printing a wide range of cloths, at present difficult to print, by incorporating soluble threads during weaving has been suggested [2]. The previous publication [8] proposed the metal carboxymethylcellulose fibers as an American counterpart of the alginate fiber. However, to our knowledge, there has been no commercial production of this fiber. From the large number of queries received from domestic commercial firms about soluble yarns, it is apparent that the textile industry is very much interested in doing at least experimental work with such yarns. Since there was no commercial production of the metal carboxymethylcellulose fiber and because of the diverse requirements for a variety of uses, we turned our attention to the possibility of modifying cotton to make a soluble yarn. It was felt that such a process, if successful, would be flexible in that the treated cotton yarn could be of the count and twist desired. Also, this type of modified cotton yarn would have the advantage over the metal carboxymethylcellulose fibers of being nontoxic, a property which is essential for use in connection with food products.

Consideration was given to the various methods of making cellulose soluble. One method of preparing completely soluble cotton yarn has been oxidation

with nitrogen dioxide [12, 13]. A soluble gauze for dressing wounds, made by this method, has been on the market for some time [4]. This gauze, left in the wound, is gradually dissolved at the pH of the blood. A rather large loss of strength with continuing degradation is reported for this product.

Also, it is reported that sodium cellulose sulfate is another soluble derivative of cellulose, and water-soluble fibers have been spun from this material [11].

In addition, a number of cellulose ethers are soluble. For example, the methyl, the hydroxyethyl, the sulfo-ethyl, and the sodium carboxymethyl ethers of cellulose were considered because they have been reported to be soluble under various conditions, depending mainly upon the degree of etherification. After preliminary trials, the carboxymethyl ether was selected for further investigation, particularly because it is nontoxic [10] and acceptable in many foods by the Food and Drug Administration. This etherification reaction may be conducted in such a manner that the cellulose is only slightly degraded and the chemicals and conditions used are such that commercial production, in a manner similar to skein mercerization, should be feasible.

Surprisingly enough, the preparation of alkali-soluble sodium carboxymethylcellulose yarns by a process using alkali to carry out the etherification is possible because the sodium carboxymethylcellulose formed is insoluble in the strong sodium hydroxide used to carry out the reaction. When excess alkali is washed out of the modified cotton with alcohol, in which the product is also insoluble, the yarn retains its fibrous form and many of its physical characteristics, except that it now disintegrates in water.

It is appropriate here to give a brief account of a typical preparation. Either a single-step or a double-step process may be used, but in preliminary work it is more satisfactory to use the latter. The first part of the treatment is carried out on solvent-extracted or kier-boiled yarn in skein form. The skein is impregnated with a water solution of 15% monochloroacetic acid containing about 0.1% of a wetting agent and is then centrifuged or squeezed to about 50% retention (on the weight of the yarn) and immersed in a 40% sodium hydroxide solution. The skein should remain in this condition for about 30 min., although this phase of the reaction can be carried out in less than a minute if the temperature is raised to about 50°–60°C. The skein is then centrifuged to remove excess caustic and is washed, first with alcohol and then with alcohol containing acetic acid. It now has a substitution of about 1 carboxymethyl group per 15 glucose anhydride units. The skein is then partially dried and rewound under slight tension before drying is completed. This gives products like those described previously [6, 7].

In the second step of the treatment, the skein is carboxymethylated to the soluble state by impregnating with 55% monochloroacetic acid as before, and squeezing to 50% retention. It is next immersed in 50% sodium hydroxide solution for 30 min., during which time the temperature rises to 40°–50°C. It is important to have the ratio of caustic to thread approximately 8:1 so that the temperature and treatment throughout the skein will be uniform. The skein is centrifuged or squeezed to remove excess alkali and then extracted with ethyl or methyl alcohol. The remaining alkali is neutralized by acidifying with acid in alcohol. In the laboratory, it is most convenient to use acetic acid for this step. The skein is then washed with hot alcohol. The material should have now approximately 1 carboxymethyl group per 2 to 3 glucose anhydride units. It is necessary to treat the product with 2% hydrochloric acid in alcohol if all of the sodium carboxymethylcellulose is to be converted to the acid form. Salts may be made with varying properties, according to the substituent. Treatment with ammonia in alcohol, for example, gives a salt which will disintegrate in distilled water. Care must be taken not to leave residues of hygroscopic salts, such as ammonium acetate, in the product, since the water absorbed will then decrease the strength of the thread.

The treated yarn generally retains from 80% to 100% of the tensile strength of the original cotton yarn from which it was prepared. On disintegration in water, a portion of the primary wall and some insoluble fibrils remain which are often rather difficult to remove when the soluble thread has been woven into a fabric. Nevertheless, 40's 2-ply yarn has been prepared which was woven into cloth and then removed satisfactorily by washing.

In summary, therefore, in addition to the preparation of the metal carboxymethylcellulose fiber by precipitation spinning, as previously described, soluble yarns can be prepared in the laboratory by the partial etherification, particularly carboxymethylation, of cotton yarns in fibrous form. We are not

aware of any commercial production of these yarns; however, small samples of the modified cotton yarn may be obtained from this Laboratory for examination.

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Book Reviews

Organic Chemistry. Paul Karrer. Fourth English Edition. Translated by A. J. Mee. New York, Elsevier Publishing Co., Inc., 1950. 973 pages. Price, $8.50.

(Reviewed by W. P. Utermohlen, Jr., The Permutit Company, Birmingham, N. J.)

This new English edition represents a revision and enlargement of the preceding version in accordance with the eleventh German edition, and is claimed to cover the results of investigations into 1949. Sections on the following subjects, among others, have been added: polysiloxanes and other organosilicon compounds, streptomycin, diacyl peroxides and peracids, and organic compounds containing isotopic atoms. Many other sections have been altered to bring them into accord with recent developments. In general, however, the classification and arrangement of subject matter is very similar to that of previous editions, again with special emphasis on naturally occurring compounds; as a result, this edition has the same merits and shortcomings typical of its predecessors.

This book is probably the most comprehensive and best single-volume textbook on organic chemistry. It affords an excellent blend of information on synthetic methods; determination of constitution; sources and uses of compounds of biological interest; stereochemical problems; and various specific fields, such as dyes, quinones, and alicyclic compounds. If one had to learn descriptive organic chemistry from a single textbook, this would be the book of choice. The book is excellent mechanically, with good paper, typography, and presentation of structural formulas.

Some deficiencies exist, however, and must be mentioned. Reviews of earlier editions have pointed out the failure to cover modern physical organic chemistry adequately, a failing which exists for the present edition also. Reaction mechanisms and kinetics, molecular rearrangements, the contributions of structural variations to reactivity, and free-radical initiated polymerizations and other reactions, for example, are not covered adequately in a textbook of the prestige associated with this one. The important specific fields of synthetic high polymers and of modern hydrocarbon-based industrial organic chemistry are scarcely mentioned.

Despite these shortcomings, however, Karrer's book should continue to be of great interest and value to advanced students and research workers, particularly those in university and biochemical laboratories.

Technique of Organic Chemistry. Vol. III. Edited by Arnold Weissberger. New York, Interscience Publishers, Inc., 1950. 661 + ix pages. Price, $10.00.

(Reviewed by Charles H. Lindsley, American Enka Corporation, Enka, North Carolina)

This excellent volume, the third in a series covering the techniques used in the investigation and preparation of organic compounds, is highly recommended to all laboratory chemists and chemical engineers. Its 8 chapters deal with procedures which are used daily in the laboratory and pilot plant, and although the applications given are to organic materials, little or no extension is required to make them equally suited to most types of materials encountered. In each chapter there is a judicious mixture in presentation of basic principles and general considerations, descriptions of the kinds and uses of commercially available equipment, and discussions of the requirements of apparatus for special purposes. These last, with the accompanying tables or charts of pertinent data, are adequate in many cases to enable the chemist to design and assemble or have built in the laboratory shop the special apparatus for his particular problem. The advantages and disadvantages of the various methods and equipment are presented, and the factors which should govern the choice in each case are discussed from a practical standpoint.

The chapter headings will indicate the scope of the book: Heating and Cooling (98 pp.), Mixing (43 pp.), Centrifuging (28 pp.), Extraction and Distribution (141 pp.), Dialysis and Electrodialysis (49 pp.), Crystallization and Recrystallization (122 pp.), Filtration (119 pp.), and Solvent Removal, Evaporation, and Drying (30 pp.). Each is written by a man or men who are thoroughly competent in the field. Throughout the book are many references (over 1,600 in all) to the literature, mostly periodical, for theory and general methods, for special ap-

paratus and methods, and for specific applications. General references at the end of each chapter will direct those interested in detailed treatment of the several topics to compendiums, monographs, and textbooks. Numerous line drawings and pictures of equipment are included.

The index appears to be excellent: principles, methods, equipment and apparatus, and compounds or groups of compounds used as agents in the various processes described are listed.

The editor, collaborating experts, and publisher are performing a valuable service to chemists and chemical engineers in preparing this series; the present volume will be found a very useful addition to any technical library.

Deformation and Flow. An Elementary Introduction to Theoretical Rheology. Markus Reiner. London, H. K. Lewis & Co., Ltd., and New York, Interscience Publishers, Inc., 1949. 362 pages; 94 illustrations; 21 tables. Price, $6.50.

(Reviewed by Earl K. Fischer, National Bureau of Standards, Washington, D. C.)

The contributions of Markus Reiner to rheology are unique. As an expert mathematician, he views deformation and flow in terms of ideal states, considering matter to be isotropic and homogeneous (for which he has been criticized, however) and capable of classification into relatively simple categories. As a practical physicist and engineer, he is concerned with the flow of asphalt mixes, deformation of concrete beams, and properties of rubber sols, as well as with the instrumental means for measuring complex flow properties. From these disparate viewpoints he has endeavored to bring system into rheological inquiry. Different schools of thought are inevitable, particularly since source material is drawn from different industries, and Dr. Reiner's writings deserve the most careful study. The present book is subtitled "An Elementary Introduction," but it is decidedly not that; instead, it is a scholarly, though eclectic, discussion of the principles of mechanics which apply to rheological measurement and analysis, documented with practical examples.

The book opens with an account of strain, deformation, viscous flow, and departures in flow from the Newtonian model. There is a discussion of the principles of measuring methods, including an important section on the rotational cylindrical viscometer, and means for analyzing rheological data. The controversial subject of "power laws," as expressions for stress-strain behavior, is resolved by considering these formulas as being useful primarily for interpolation. Additional chapters cover tension and extension, work-hardening, bending and torsion, creep, elastic-viscous effects, strength, and dilatancy. Numerous diagrams and a consistent system of mathematical notation facilitate exposition of these topics.

Unlike most modern books, the text is written informally in the first person, and the reader gains a pleasant immediacy with the subject. The book is noteworthy, also, for its historical perspective: the author was a part of the scientific developments he describes, and side lights on the work of his contemporaries, always graciously given, provide in themselves interesting reading. This book will prove of value to all investigators concerned with deformation and flow phenomena. The reader who wishes to follow Dr. Reiner's work should consult also his "Twelve Lectures on Theoretical Rheology" (1949).

Industrial Textiles Directory. Daily News Record. New York, Fairchild Publications, Inc., 1950. 133 pages. Price, $2.00.

The 1950 edition of the annual directory of textiles and their manufacturers and distributors reflects the rapid increase in the production and utilization of synthetics. To the "Other Man-Made Fibers, Yarns, and Fabrics Section" have been added: Nylon Spun Yarns; Spun Nylon Fabrics; Orlon Fabric; Fiber "V" Yarn and Staple; Vinyon "N" Multifilament Fabric; and Dynel Staple, Spun Yarn, and Fabric. New also are a section devoted to plastic and film sheeting, with a chapter on converters of plastic film, and a section on coated fabrics.

This is an important publication and should be helpful to all those concerned with cotton and synthetic textiles. Although it would be a major undertaking to develop and add a similar directory of woolen products and manufacturers, if this were done the publication would be much more truly an "Industrial Textiles Directory."

Information for Contributors

to

TEXTILE RESEARCH JOURNAL

REQUIREMENTS FOR COPY submitted to the TEXTILE RESEARCH JOURNAL conform, in general, with those for other scientific publications. This outline is intended to point out several differences and to assist authors with certain details required in the preparation of their papers. Observance of these style requirements will materially assist the editors.

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The JOURNAL seeks to cover the broad field of textile research with papers on pure science, engineering, and technology. It is equally interested in studies relating to chemistry, physics, and physical chemistry.

Types of Papers.—There are five principal classes of contributions which are acceptable to the JOURNAL:

1. Scientific articles on fundamental research.
2. Technical papers on applied research (grouped in the "Industrial Section").
3. Reports on laboratory techniques and new instruments.
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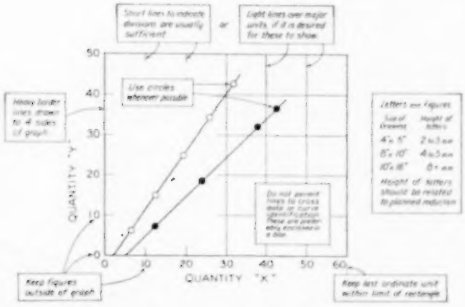
Equations.—All equations should be verified by the author; alterations which require hand-resetting of type are expensive. Exponents and subscripts should be legible and properly positioned. There should also be a clear distinction between small and capital letters, and there should be no possibility of confusing the small letter "l" (el) with the figure "1" (one), or the letter "O" with zero, etc. Complicated structural formulas should be submitted in the form of carefully made India-ink drawings; symbols and Greek letters should be written clearly; if there is any question about legibility, it is advisable to spell out the name of the symbol in the margin and circle the instructions with pencil.

Description of Experiments.—The apparatus and procedures used should be described and illustrated in sufficient detail to enable other investigators to repeat the experiments. Data should be included to substantiate the conclusions that are drawn. A concise treatment is important, nevertheless. Frequently, curves are sufficient, without tabulation of the same data.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(Measurements on Rotational Viscometer: Maximum Rate of Shear, 100 sec^{-1}; Temperature, 30° ± 0.1°C)

For arrangement, see tables in current issues of the JOURNAL.

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